suggested for the rearrangements in monoaryltellurium tris(diethyldithiocarbamates).

The single crystal X-ray structure determination of (4-ethoxyphenyl)tellurium trichloride reveals that the compound crystallizes as a polymer propagated in [001] direction with approximate square-pyramidal coordination of each tellurium atom. The tellurium atoms are linked through a single bridging chlorine. The crystal data are: space group orthorhombic, $P2_1am$, $\underline{a}$ = 13.427(3), $\underline{b}$ = 11.767(2), $\underline{c}$ = 7.425(1) Å, $\underline{\alpha}$ = $\underline{\beta}$ = $\underline{\gamma}$ = 90.00°, $\underline{v}$ = 1173.12 Å^3.

The (4-ethoxyphenyl)tellurium tribromide exhibits a dimeric structure. The two approximately square-pyramidal tellurium coordination polyhedra are cis-fused through two bridging bromine atoms. The dimeric units are further arranged in pairs, square-pyramids base-to-base. The crystal data for the compound are: space group triclinic, $P\bar{1}$, $\underline{a}$ = 10.280(4), $\underline{b}$ = 11.029(8), $\underline{c}$ = 11.715(6) Å, $\underline{\alpha}$ = 71.92(5), $\underline{\beta}$ = 102.01(5), $\underline{\gamma}$ = 99.29(5)°, $\underline{v}$ = 1121.71 Å^3.

To My Parents

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ACKNOWLEDGEMENTS

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CHAPTER I. GENERAL INTRODUCTION

Tellurium is well known to form organometallic compounds. However, its organic chemistry has not been previously investigated as extensively as that of sulfur and selenium. The unusal properties, toxicity and chemical behavior of most organotellurium compounds often make systematic studies quite challenging and have discouraged previous workers from attempting to probe into this potentially important area. The differences in the chemistry of organosulfur, selenium, and tellurium can partly be understood on the basis of physical and chemical constants which change from one element to other. Some fundamental properties of the elements S, Se and Te are summarized in Table I-1.

In general, organotellurium compounds are less thermally stable compared to analogous organo-sulfur and -selenium derivatives. The Te-Te bond is distinctly less stable and is readily cleaved in many reactions. In organosulfur chemistry particularly, corresponding cleavage reactions of S-C and S-S bonds are usually slower, allowing for more frequent isolation of intermediates.

The bond energies between tellurium and elements X with high electronegativity are larger than those between bonds of sulfur or selenium with the same elements (e.g., S-X, Se-X, and Te-X; where X = halogens). The ionic character of element-halogen bonds also increases in the order Te-X < Se-X < S-X. Conversely, the bond energies

Table I-1

Some fundamental properties of S, Se and Te

Property \ Element		S	Se	Te
Atomic number		16	34	52
Atomic weight		32.06	78.96	127.60
Electronic configuration		$(Ne)3s^2p^4$	$(Ar)4s^2p^4$	$(Kr)5s^2p^4$
Single bond covalent radii, Å		1.04	1.17	1.37
Tetravalent covalent radii, Å		1.04	1.14	1.32
Octahedral covalent radii, Å		-	1.40	1.52
Van der Waals radii, Å		1.85	2.00	2.20
Radius of negative ion (M^{-2}), Å		1.86	1.98	2.22
Radius of positive ions, Å				
M^{+4}		0.53	0.69	0.89
M^{+6}		0.30-0.34	0.35	0.56-0.61
Ionization energies	I	238.91	224.89	207.76
Kcal/mol[a]	II	538.01	488.66	428.93
	III	803.21	710.74	644.79
	IV	1090.78	990.24	862.71

Table I-1 (Contd.)

Electronegativity			
Pauling[b]	2.58	2.55	2.10
Sanderson[c]	2.66	2.76	2.34
Allred and Rochow[d]	2.44	2.48	2.01
Mulliken and Jaffe[e]			
p	2.28	2.18	3.08
sp^3	3.21	3.07	3.04
Electron affinity[f]			
$E\text{-}E^{-1}$	2.07	2.11[g] 2.20[h]	2.30[h]
$E\text{-}E^{-2}$	-6.10	-4.40	-
Bond energies, Kcal/mol			
E-C	59	50	-
E-E	64 ± 5	41	30[i]
E=E	101.5 ±1.5	65	52.2
E-F	68	68.1	78.8
E-Cl	-	46	74.3
E-Br	-	36	42
E-H	87.7	66	57

a Ref. 1; b Ref. 2; c Ref. 3; d Ref. 4; e Ref. 5; f Ref. 6; g Ref. 7; h Ref. 8; i Ref. 9.

between tellurium and elements having a low electronegativity are lower than those between sulfur and selenium with the same elements (e.g., S-H, Se-H and Te-H). This explains the increasingly acidic character of phenol analogs in the series Te < Se < S < O.

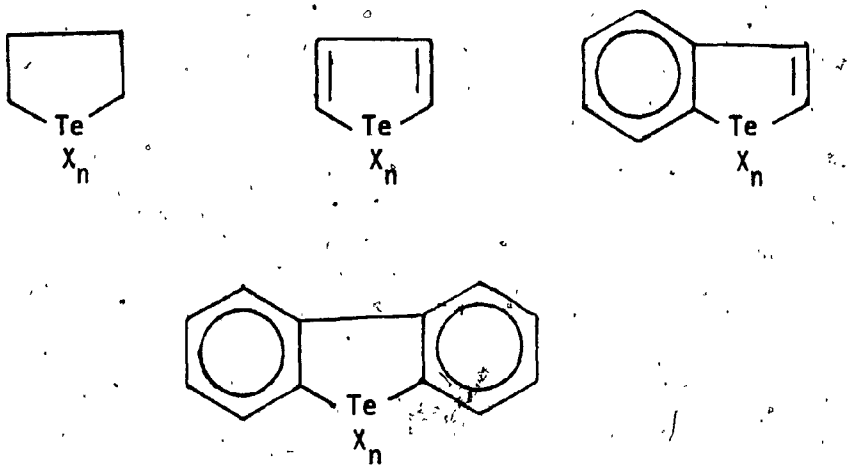
Organotellurium chemistry forms part of organometallic chemistry which is flourishing at present. Its history dates back to 1840 when Wöhler (10) reported the synthesis of the first organotellurium compound. In the decade between 1910 and 1920, Lederer (11) broadened this area of research by synthesising a large number of aryltellurium compounds. In 1920 Morgan, Drew and coworkers (12), began exploring the chemistry of five- and six-membered heterocyclic ring systems of tellurium. Since then, the literature has grown rapidly, and several excellent reviews have been written on various aspects of organotellurium chemistry (13-25). Outstanding among these is the review of Irgolic and Zingaro (25) or the book by Irgolic (26) which thoroughly covers the chemistry and the reactions of organotellurium compounds known to 1971. The period 1971-1978 has been surveyed by Irgolic and appears in the Annual Survey Series of the Journal of Organometallic Chemistry (27).

The vast majority of organotellurium compounds fall into the following four major classes having the general formulae:

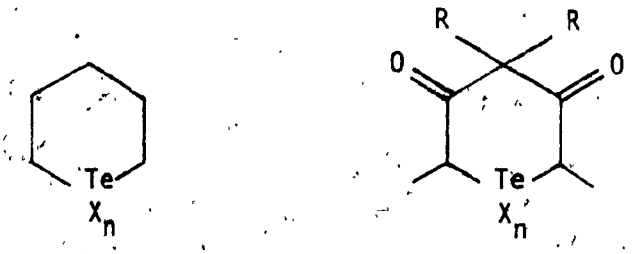
1. R_nTeX_{2-n} ($n = 1$ or 2)
2. R_2Te_2
3. R_nTeX_{4-n} ($n = 1, 2, 3$ or 4)

4. Heterocyclic tellurium compounds

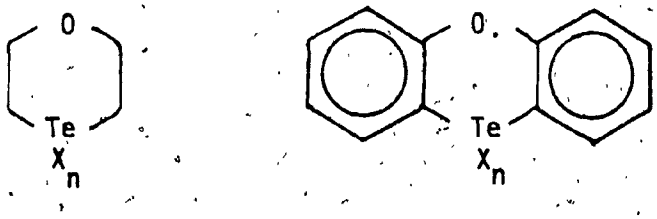
a) Five-membered ring system:



b) Six-membered rings with Te as the heteroatom:



c) Six-membered rings with Te and either O, S, or Se as the heteroatoms:



where R may be alkyl or aryl groups and X ranges from electronegative groups such as OR, OCOR, halogen, pseudohalogens, other acid radicals through, neutral ligands such as H, to electropositive atoms such as Li or Na. A few tellurium analogues of aldehydes and ketones are known, in addition to organotellurium compounds containing a tellurium-metal or a tellurium-metalloid bond, and Lewis acid-base adducts of the type $R_nTeX_{4-n}.L$ (n = 0 or 1) or $R_2Te \longrightarrow$ Metal salt. In this last class the metal is usually a transition metal.

NATURE OF BONDING

Tellurium(II) derivatives:

The tendency of tellurium(II) in its complexes is towards square-planar four coordination. A series of tellurium(II) complexes exists, where stereochemistry, bond lengths, and trans effects of ligands indicate that bonding is of the three-centre, four-electron type (28,29). Two of the p-orbitals (p_y and p_z) of dipositive tellurium each participate in linear, three-centre bonding with two ligands so that two such systems are formed at right angles (Figure I-1). A list of some tellurium(II) complexes exhibiting angles close to 90° is presented in Table I-2 and a structure of $[Te(thiourea)_4]^{2+}$ as a typical example is shown in Figure I-2.

In complexes of the type TeL_2X_2 (L = thiourea, ethylenethiourea, trimethylenethiourea or tetramethylenethiourea; X = Cl^-, Br^-, I^-, thiocyanate, selenocyanate, methanethiosulphonate, and benzenethio-

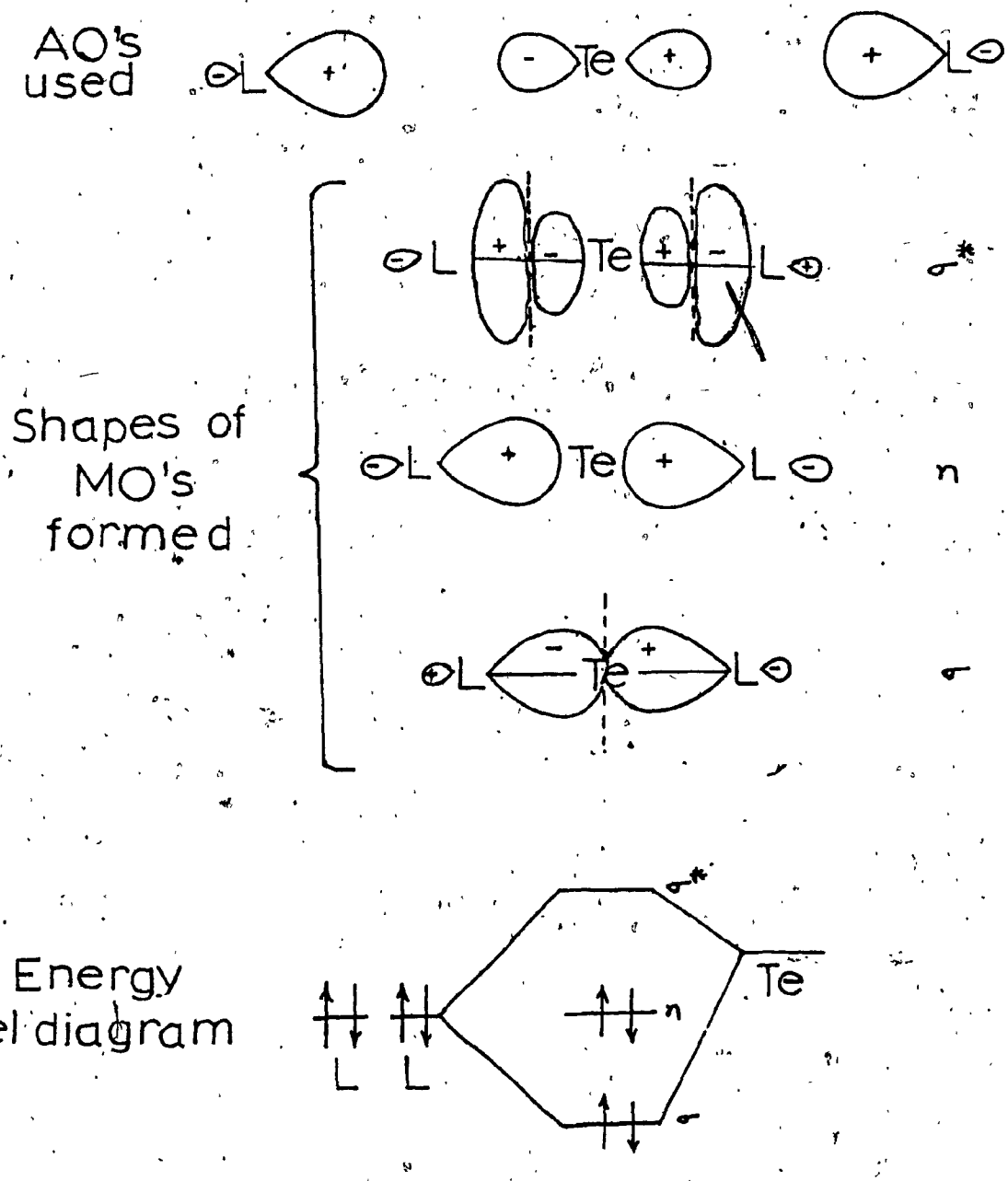


Figure I-1: Molecular orbital representation of three-centre four-electron bonding (L = Ligand)

Table I-2

X-ray data for tellurium(II) compounds showing angles close to 90°

Compound	Angle	(°)	Reference
$Te(tu)_4Cl_2$	S-Te-S	90.6	30
$Te(tu)_4Cl_2.2H_2O$	S-Te-S	90.3	30
$Te(su)_4Cl_2$	Se-Te-Se	90.3	31
trans-$Te(etu)_2Br_2$	S-Te-Br	89.2	32
trans-$Te(etu)_2I_2$	S-Te-I	89.2	32
trans-$Te(etu)_2(SCN)_2$	S-Te-S	90.1	29
trans-$Te(etu)_2(SeCN)_2$	S-Te-Se	89.9	29
trans-$Te(tu)_2(S_2O_2CH_3)_2$	S-Te-S	90.6	33

tu = thiourea; su = selenourea; etu = ethylenethiourea.

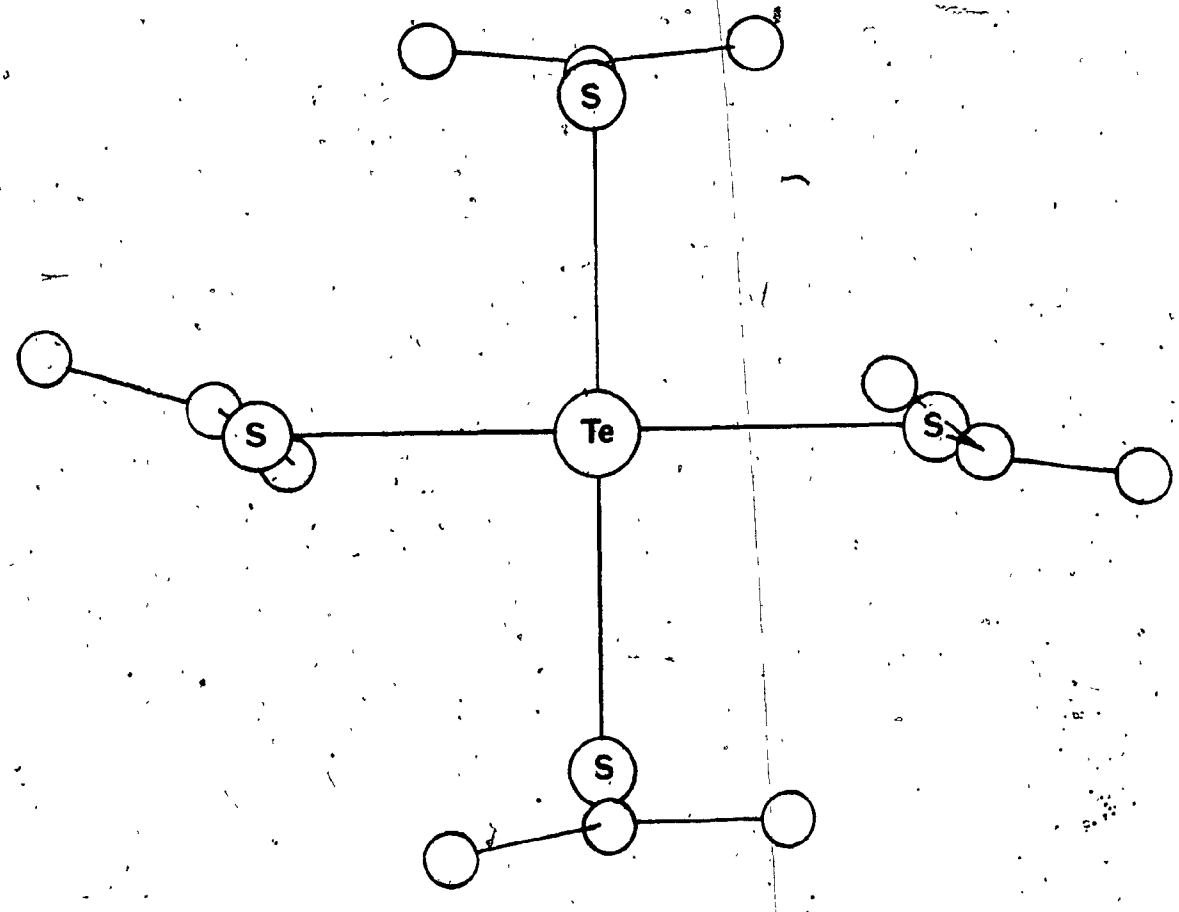


Figure I-2: The molecular structure of $[Te(thiourea)_4]^{2+}$ (30)

sulphonate), cis-trans isomerism is also possible. Foss (28) suggested that the tendency towards trans configuration increases with increasing softness (34) of the ligand, from chloride through bromide to iodide, and from thiocyanate to selenocyanate.

Two- and some four-coordinate inorganic and organotellurium(II) compounds, where the angle between two ligands varies significantly from its ideal value 90°, are also known (Table I-3). On the basis of Mössbauer (35-38) data, it was suggested that this may be due to the direct participation of some fraction of the 5s electrons in the bonding. Cheyne et. al. (35,36) and Jones et. al. (37) reported that the amount of s-character in the bonds formed by divalent tellurium is determined by the nature of other atoms present. From the data, it appears that the s-admixture could vary from a small percentage to that required for sp^3 hybridization. Aleksandrov et. al. (39), apparently unaware of the earlier structural work of Foss et. al. (29,31), interpreted their results from Mossbauer and infrared studies on some divalent tellurium complexes in terms of a tetrahedral geometry.

Tellurium(IV)- and Tellurium(VI) derivatives:

With the exception of oxygen, all the elements of the group can employ their relatively low-lying energy d-orbitals to increase their valence and coordination number above two. With a certain expenditure of energy, which is compensated by energy liberated during covalent bond formation, it is possible for tellurium to assume

Table I-3

Bond angles in inorganic- and organotellurium(II) compounds

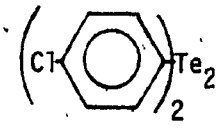
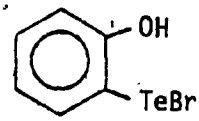
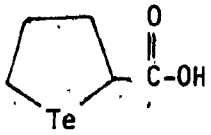
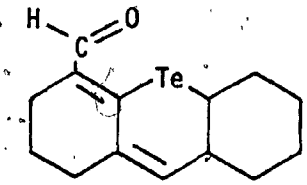
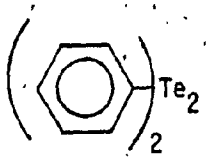
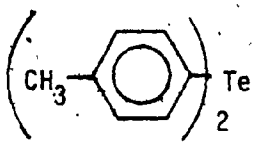
Compounds	Bond angle	(°)	Reference
trans-$Te(etu)_2(S_2O_2CH_3)_2$			
triclinic dimorph	S-Te-S	91.6	31
monoclinic dimorph	S-Te-S	92.6	31
cis-$Te(tu)_2Cl_2$	S-Te-S	93.0	40
	Cl-Te-Cl	93.0	
cis-$Te(tu)_2Br_2$	S-Te-S	95.0	40
	Br-Te-Br	93.0	
	C-Te-Te	94.0	41
	C-Te-Br	94.2	42
	C-Te-C	94.1	43
	C-Te-C	94.0	44
$TeBr_2$	Br-Te-Br	98.0	45
$[(CH_3O)_2PS_2]_2Te$	S-Te-S	98.3	46

Table I-3 (Contd.)

	C-Te-Te	98.8	47
$(CH_3 \cdot SO_2 \cdot S)_2Te$	S-Te-S	100 ± 3	48
$[(C_2H_5)_2P(S)Se]_2Te$	Se-Te-Se	100.7	49
	C-Te-C	101 ± 2.7	40
$Rb_2Te(S_2O_3)_2$	S-Te-S	101.1	31
$(NH_4)_2TeS_4O_6$	S-Te-S	103 ± 2	51
Te (elemental)*	Te-Te-Te	103.7 ± 2	52

etu = ethylenethiourea; tu = thiourea

* crystallizes in hexagonal system.

an excited state by promoting 5s and 5p electrons to the empty 5d-orbitals. Thus, the tetravalency of tellurium is derived from a hypothetical sp^3d square-pyramidal or trigonal-bipyramidal hybridized valence state with the fifth position in the resulting geometry occupied by the lone-pair. In tetravalent derivatives, where the coordination number of tellurium exceeds four, further utilization of d-orbitals occurs. This is exemplified by rare six, seven and eight coordinated complexes: In $PhTe(SCSN(C_2H_5)_2)_3$ (53,54) and $Te(SCSN(C_2H_5)_2)_4$ (53) the coordination number for Te is 7 and 8, respectively.

In some tellurium(IV) octahedral complexes, e.g., $[TeCl_6]^{2-}$, $[TeBr_6]^{2-}$, and $[TeBr_4.2((Me_2N)_2C{=}S)]$, the seventh electron pair on the tellurium atom is stereochemically inactive (55-58). Such an inactive pair is found also in $[SbCl_6]^{3-}$, IF_6^-, and XeF_6 (59-63). This stereochemical inactivity of unshared electron pairs in octahedral complexes has been explained as resulting from the small overlap of the valency shell ns orbital with the ligand a_{1g} orbital set (Figure I-3) (64,65). Thus, according to Urch (63), the seventh electron pair goes into the a^*_{1g} low energy antibonding MO. This MO is mostly localized on the ligands and thus electrons in this orbital do not disturb the octahedral arrangement of the six bonding pairs (64).

By analogy with sulfur and selenium derivatives, in organotellurium(II) and (IV) compounds bonding of the type $d\pi$-$p\pi$ or $p\pi$-$p\pi$ is also plausible. Few such interactions have been reported: on the basis of dipole moment and nmr data (66), it was shown that in

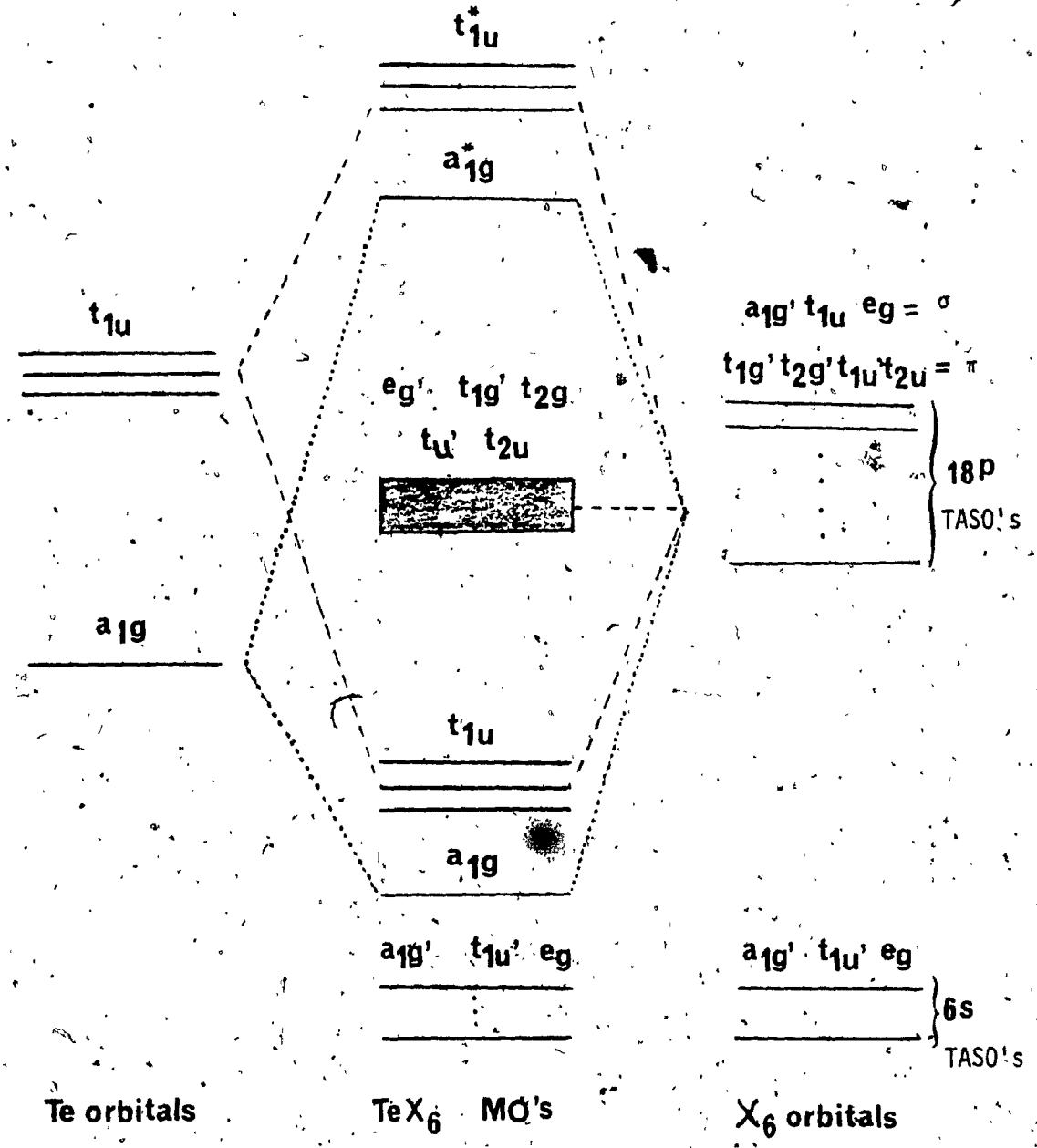


Figure I-3: The simplified molecular orbital energy diagram for $[TeX_6]^{2-}$

diaryltellurides no p_{Te}-π bonding occurs unless a strong electron acceptor substituent, such as a nitro group, is present, whereas with powerful π-donors such as a $(CH_3)_2N$- group para to tellurium, an interaction of the type $5d_{Te}$-π ring and p_{Te}-π ring was observed. A similar investigation of a large number of symmetrical and unsymmetrical diaryltellurium dihalides led to a similar conclusion (67).

CHAPTER II. SYNTHESIS

SECTION A: PREPARATION OF MONO- AND DIORGANOTELLURIUM(IV) CHLORIDES

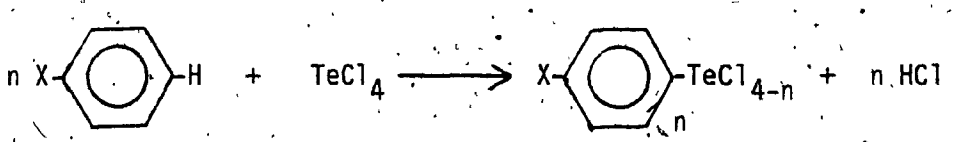
INTRODUCTION

In recent years considerable interest has been shown in the synthetic aspects of organotellurium halides. The profound interest in the field may be attributed to the purely practical need for improving the properties of materials in photographic and biological processes and creating hitherto unknown compounds or preparing known compounds by rather simpler methods. The diaryltellurium dichlorides have been shown to possess a remarkably strong antibacterial action (68), while a variety of trichlorides and dichlorides have been found very useful in light-sensitive, thermally developable systems (69) and in producing direct positive images (70-74). Recently, bis(benzoylmethyl)tellurium dichloride (75) has found use as a photoinitiator in the polymerization of methylmethacrylate under conditions which vigorously exclude ionic processes. The use of dimethyltellurium diiodide (76) and mono- and diaryl-tellurium chlorides (77) in the preparation of $RNHCOOCH_3$ and the corresponding carboxlic acids, respectively, have also been described.

Though the first synthesis of organotellurium halides was reported in 1884 by Shimose (78), the interest in this class of organotellurium compounds has increased only in the past few decades.

The subject has been adequately reviewed by Rheinbholdt (18), Petragnani and Compos (23) and in a monograph (24) and a book (26) by Irgolic.

A critical survey of the literature reveals that only a few methods are known that produce mono- and di-aryltellurium chlorides in good yield. Morgan et. al. (79,80) and others (81-86) reported that the benzene derivatives containing RO-, RS-, HO-, R_2N-, RCONH-, 2-quinolyl- or 9-acridinyl as an activating group react with tellurium tetrachloride upon heating on a water bath without solvent to give mono- or di-aryltellurium chlorides in good yields:



X = activating group
n = 1 or 2 (II-A-1)

However, in an analogous reaction, $TeCl_4$ forms adducts when X is the $(CH_3)_2N$- or $CH_3(Ph)N$- group (87). $TeBr_4$ and TeI_4 were found inert (24) or shown to produce bromo- or iodo derivatives of aromatic compounds (86). Ogwa et. al. (88), Sadekov et. al. (89), and Bergman (90) extended the range of aromatic compounds found to react via

reaction II-A-1. In most cases, a poor yield of trichloride or dichloride was obtained. With chlorobenzene and benzonitrile, a mixture is reported (90).

Recently, Gupta et. al. (91) showed that (4-dimethylphenyl)tellurium trichloride can be synthesised in high yield by heating $[(CH_3)_2NHC_6H_5]_2TeX_6$ or $TeX_4.2C_6H_5N(CH_3)_2$ (where X = Cl, Br or I).

Bergman (90) and Gunther et. al. (92) suggested that the combination of tellurium tetrachloride and aluminium trichloride constitutes an efficient reagent for introducing tellurium into the benzene and higher analogues. However, a recent report by Albeck and Shaik (93) indicates that although the presence of aluminium trichloride or silver nitrate as Lewis acid indeed accelerates the reaction, the preference for chlorination vs. telluration depends on factors such as the polarity of solvent, the nature of R and X groups and the specificity of organic compounds.

In past (24-26) and recent years (27), a method which has been widely used to prepare mono- or di-aryltellurium(IV) halides involves the treatment of a halogenating agent with diaryltelluride or diarylditelluride. It is useful only when the starting tellurides or ditellurides can be synthesised from sodium telluride or sodium ditelluride and an organic halide.

Several contradictory reports have also been published on the synthesis of organotellurium trichlorides and dichlorides from the addition reactions of tellurium halides with unsaturated organic substrates. Fischer et. al. (94) reported that tellurium tetrachloride, when treated with cyclohexene, produces elemental tellurium; however, Compos and Petragnani (95,96), Funk et. al. (97) and Ogwa et. al. (88) have isolated (2-chlorocyclohexyl)tellurium trichloride. In the reaction with styrene, Fischer (94), and Compos and Petragnani (96) observed an unidentified chlorination product, while for the same reaction Patai and Elmaleh (98) claimed the synthesis of tellurium derivatives. More recently, controversy has also arisen on the chlorination (93) or telluration (99) of anthracene and its halo derivatives.

The first paper describing the use of an organometallic compound as arylating agent for tellurium was published by Campbell and Turner (100). They treated arylmercuric chlorides with tellurium tetrachloride in dioxane to give the corresponding aryltellurium trichlorides. Farrar (101) and Rheinbholdt and Vicentini (102,103) extended this reaction to prepare a variety of other aryltellurium halides. In recent years the successful use of organo-silicon (104), -tin (105), -lead (106), and -mercury (107,108) compounds, and diphenylthallium chloride (109) have been reported. Pant (106) has shown that, in the reaction between tellurium tetrachloride and diphenyldimethyllead, tellurium tetrachloride

preferentially cleaves the lead-carbon(aryl) bond and diphenyltellurium dichloride is formed in good yields. The use of alkyllead(IV) and hexaorganodilead compounds to prepare the corresponding tellurium derivatives have not so far been investigated.

RESULTS AND DISCUSSION

Using organolead(IV) compounds

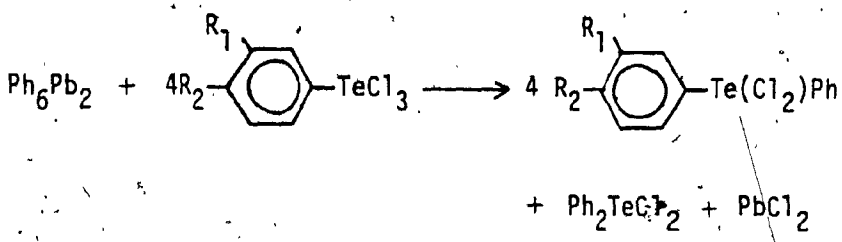
The preparation of diorgano(symmetrical and unsymmetrical)tellurium chlorides has been achieved according to reactions II-A-2 to II-A-5:

$$(CH_3)_4Pb + TeCl_4 \longrightarrow (CH_3)_2TeCl_2 + (CH_3)_2PbCl_2 \qquad \text{(II-A-2)}$$

$$(CH_3)_4Pb + C_2H_5O\text{-}C_6H_4\text{-}TeCl_3 \longrightarrow C_2H_5O\text{-}C_6H_4\text{-}Te(Cl_2)CH_3 + (CH_3)_3PbCl \qquad \text{(II-A-3)}$$

$$R_6Pb_2 + 2TeCl_4 \longrightarrow 2R_2TeCl_2 + R_2PbCl_2 + PbCl_2$$

$(R = CH_3\text{-};\ C_6H_5\text{-};\ 4\text{-}CH_3C_6H_4\text{-})$ (II-A-4)



$$Ph_6Pb_2 + 4R_2\text{-}C_6H_3(R_1)\text{-}TeCl_3 \longrightarrow 4\ R_2\text{-}C_6H_3(R_1)\text{-}Te(Cl_2)Ph + Ph_2TeCl_2 + PbCl_2$$

(R_1 = H, R_2 = CH_3O-; R_1 = H, R_2 = C_2H_5O-; R_1 = CH_3, R_2 = CH_3O-; R_1 = CH_3O-, R_2 = CH_3O-)

(II-A-5)

Various reactions, m.p.'s and yields are given in Tables II-C-3 and II-C-4 and the ^1H nmr spectra of unsymmetrical diorganotellurium dichloride products are presented in Table II-A-1. Unlike the reactions of tetraaryllead compounds (106), the reactions II-A-2 and II-A-3 with tetramethyllead proceed fairly slowly. This is probably due to the lower susceptibility of lead-carbon(methyl) bonds to cleavage by these reagents. By analogy with the mechanism of the reaction of other organometallic compounds (107), the transfer of methyl group from lead to tellurium metal can be written as given by scheme II-A-1.

Reactions of hexaorganodilead compounds with a variety of metal salts have been extensively studied. It has been suggested (110,111) that in all cases, reduction of metal salts occurs and a mixture of tetraorganolead and lead dichloride or triorganolead chloride is formed. Recently, the ready cleavage of the lead-lead bond rather than lead-carbon(alkyl or aryl) bonds in hexaorganodilead

Table II-A-1

^1H nmr spectra of unsymmetrical diorganotellurium(IV) chlorides[a]

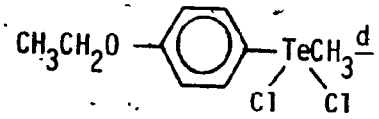
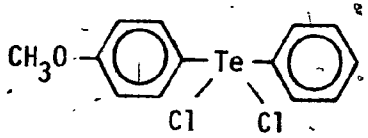
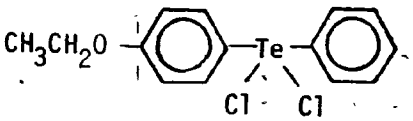
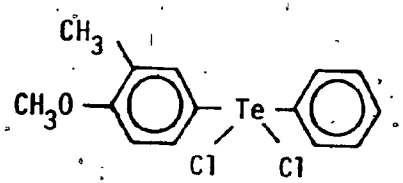
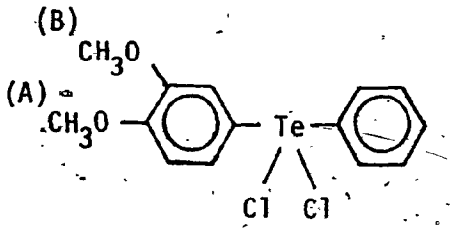
Compound	Chemical shifts[b] δ (ppm)	Multiplicity[c] and Assignment
	8.19 7.24 4.19 3.18 1.35	d; phenyl protons H-3,5 d; phenyl protons H-2,6 q; OCH_2CH_3 s; CH_3 t; OCH_2CH_3
	9.10-6.93 3.83	m; phenyl protons s; OCH_3
	8.20-6.91 4.07 1.43	m; phenyl protons q; OCH_2CH_3 t; OCH_2CH_3
	8.16-6.86 3.85 2.23	m;phenyl protons s; OCH_3 s; CH_3

Table II-A-1 (Contd.)



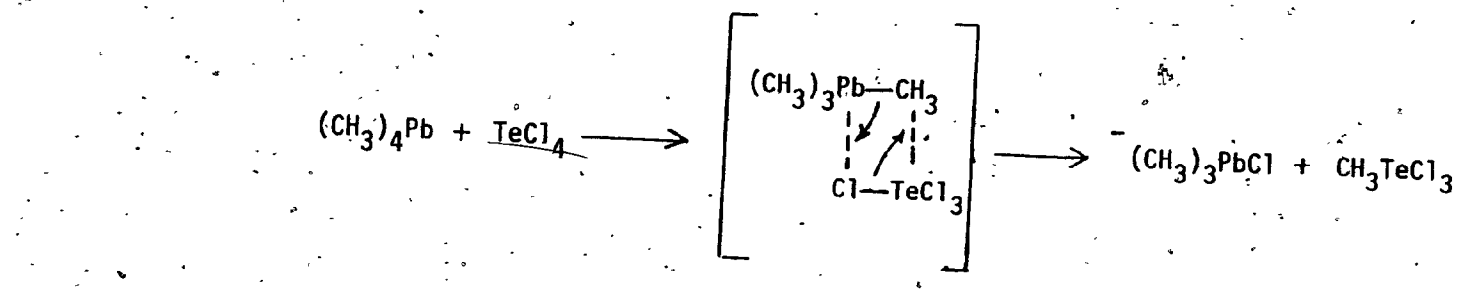
8.63-7.13	n; phenyl protons
4.03	s; OCH_3 (B)
3.93	s; OCH_3(A)

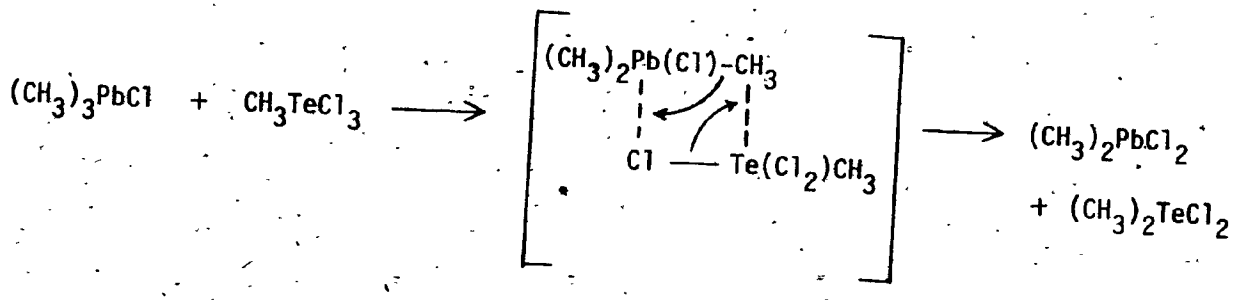
a In deuteriochloroform.

b Shift relative to TMS as internal reference.

c s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

d Spectrum in dimethylsulfoxide-d_6.


(CH3)4Pb + TeCl4
(CH3)3Pb—CH3
Cl—TeCl3
(CH3)3PbCl + CH3TeCl3

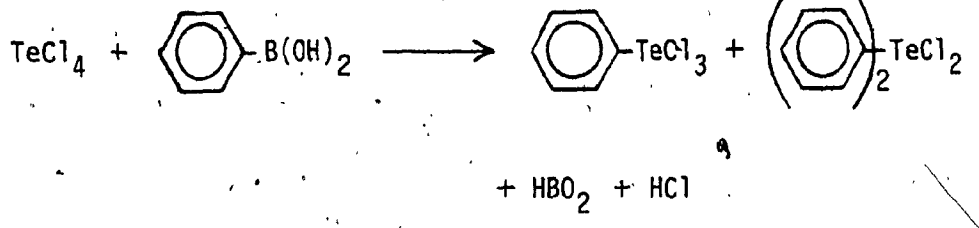

(CH3)3PbCl + CH3TeCl3
(CH3)2Pb(Cl)-CH3
Cl — Te(Cl2)CH3
(CH3)2PbCl2
+ (CH3)2TeCl2

Scheme II-A-1

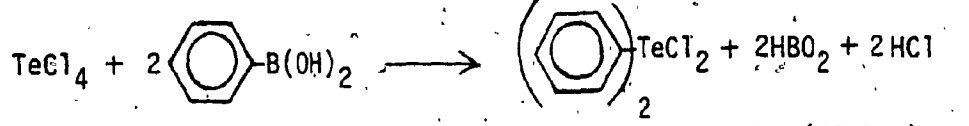
products by a variety of reagents has been shown to provide a suitable route for the synthesis of triorganolead salts (112). However, in the present study, the simultaneous cleavage of lead-carbon(alkyl or aryl) bonds by tellurium tetrachloride and monoaryltellurium trichloride (reactions II-A-4 and II-A-5) has been observed. This is in agreement with the earlier work reported by Kumar Das et. al. (113) on the cleavage reaction of hexaphenyldilead by mercuric salts.

Using arylelement(III) reagents.

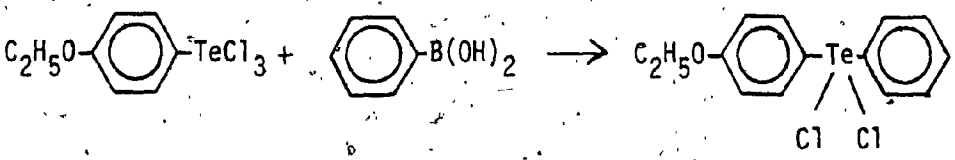
Phenylboric acid transmetallates tellurium tetrachloride or monoaryltellurium trichloride on refluxing in benzene, toluene or carbon tetrachloride to give mono- or di-aryltellurium chlorides (reactions II-A-6 to II-A-8):



(II-A-6)



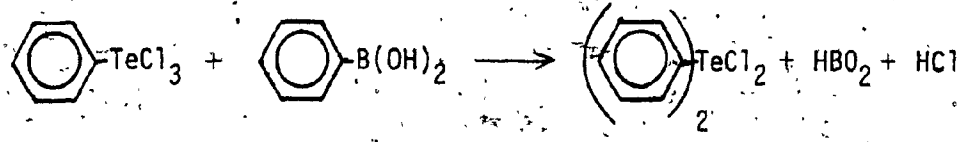
(II-A-7)



$$+ HBO_2 + HCl$$

(II-A-8)

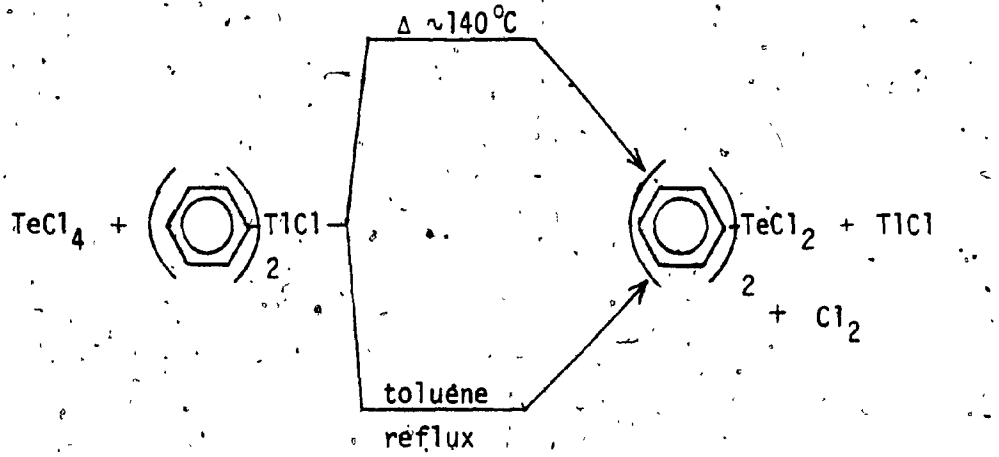
The formation of a small amount of diphenyltellurium dichloride in reaction II-A-6 is attributed to a secondary reaction occuring between the initially formed phenyltellurium trichloride and phenylboric acid (reaction II-A-9):



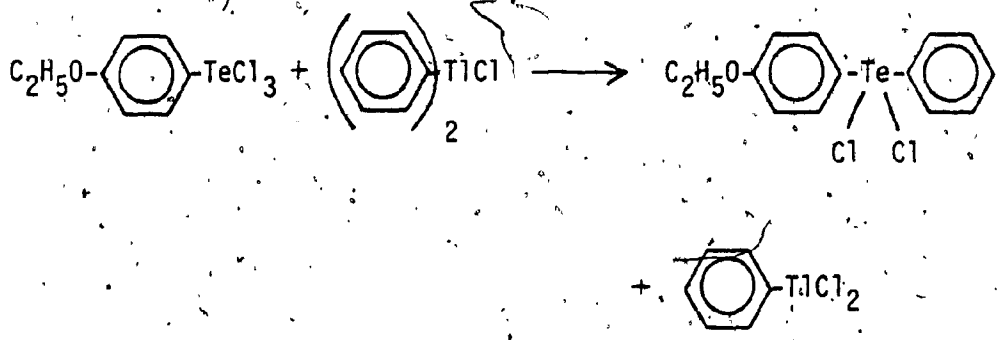
(II-A-9)

The reactions represented by II-A-7 and II-A-8 proceed to completion after reflux for about twenty hours.

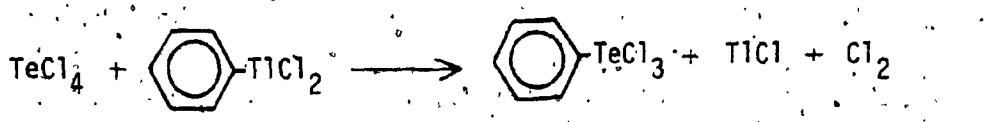
Using phenylthallium(III) chlorides, the syntheses of mono- and diaryl-(symmetrical and unsymmetrical)tellurium chlorides has been achieved according to reactions II-A-10 to II-A-12:



(II-A-10)



(II-A-11)

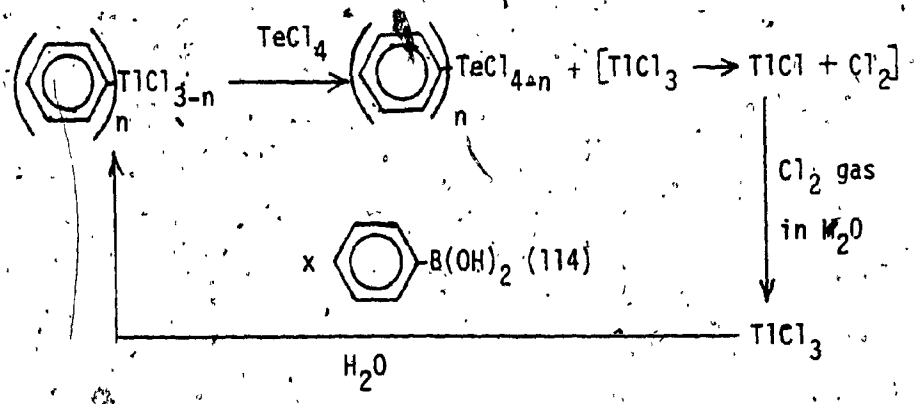


(II-A-12)

The noteworthy features of these reactions are:

1. The diphenylthallium chloride and phenylthallium dichloride are easy to synthesise (114).
2. The thallous chloride, formed as a by-product in the reactions,

can be recycled to prepare arylthallium(III) chlorides:



3. The reactions can also be employed to prepare a variety of arylsubstitutedtellurium(IV) chlorides by using appropriate mono- or di-arylthallium(III) chlorides.

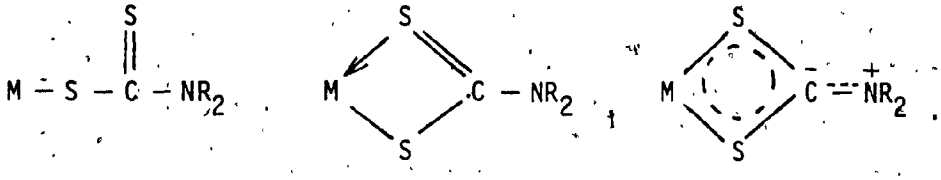
4. In addition to the unsymmetrical diaryltellurium dichlorides, reaction II-A-11 provides a suitable synthetic route for monoarylthallium(III) dichlorides.

SECTION B: PREPARATION OF TELLURIUM(IV)- AND ARYLTELLURIUM(IV)-DITHIOCARBAMATES AND BENZENETHIOLATES

INTRODUCTION

Compounds containing a covalent Te-S bond in general, and the title derivatives in particular, have received only limited attention and very few reports describing their preparation, properties, and structures have been published. Though in 1932 Murrill (115) patented some of the tellurium dialkyldithiocarbamates as accelerators in vulcanization of rubber, Glew and Schwab (116) are credited with the synthesis of tellurium tetrakis(dialkyldithiocarbamates) in 1950. Foss (117) prepared tellurium bis(dialkyldithiocarbamate) by displacing methanethiosulphonate ions of relatively stronger oxidizing capacity in the corresponding tellurium(II) derivative with bis(thiocarbamyl)disulfide. The monoaryltellurium tris-dialkyldithiocarbamates have been synthesised by refluxing a solution of bis(thiocarbamyl)disulfide and diarylditellurides (aryl = 4-methoxyphenyl) in chloroform or from the reaction between monoaryltellurium trichloride salts and the sodium salt of dialkyldithiocarbamic acid also in $CHCl_3$ (118). Recently, Srivastava et. al. (119) synthesised compounds of the general formula $R_2Te(dtc)_nX_{2-n}$ (where n = 1 or 2; R = alkyl or aryl group; dtc = N,N-disubstituted dithiocarbamate; X = Cl or I) from the reaction of the ammonium salt of dithiocarbamic acid with organotellurium(IV) halides in appropriate proportions.

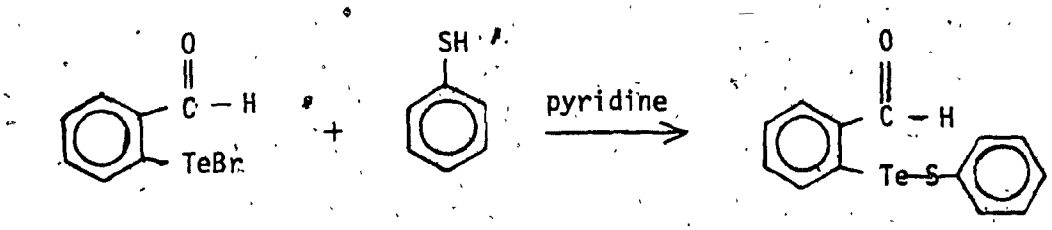
It is widely held that dithiocarbamate groups in their metal and organometal complexes behave as bidentate ligands. However, there are a few reports which indicate that the dithiocarbamate moiety may act either as a monodentate ligand (a) (120,121); or both as a monodentate (a), and bidentate (b or c) ligand (122-124):



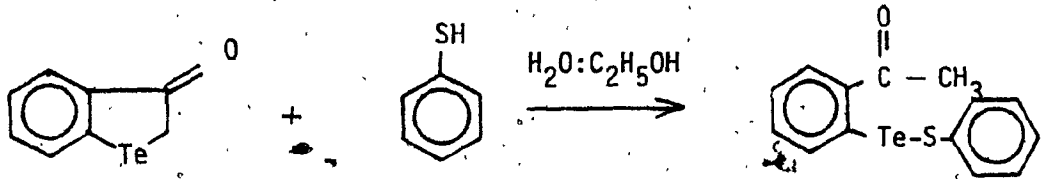
(a) (b) (c)

Esperas and coworkers (53,54) studied the X-ray crystal structures of phenyltellurium tris(diethyldithiocarbamate) and tellurium tetrakis(diethyldithiocarbamate) (53). Bidentate behavior of the diethyldithiocarbamate group was observed; thus, in the two compounds in the solid state, tellurium attains seven- and eight-coordination, respectively. Based on IR, NMR and UV spectroscopic data, Srivastava et. al. (119) tentatively assigned the ester type structure (a) to the dithiocarbamate group in $R_2Te(dtc)_2$, but a bidentate (b or c) character in $R_2Te(dtc)X$. The structures of monoaryltellurium tris(dithiocarbamate) compounds in solution and of diorganotellurium bis-dithiocarbamates in the solid state using X-ray crystallography have not yet been reported.

The arylthio derivatives of tellurium and aryltellurium were not known until 1972: Piette and coworkers (125,126) reported for the first time that aryltellurobromide or 3-oxa-1,2-dihydrobenzenetellurophene react with arylthiols in pyridine or water:ethanol mixture to give corresponding thiotelluride derivatives in good yields (reactions II-B-1 and II-B-2):



(II-B-1)



(II-B-2)

Recently, Spencer et. al. (127) extended this reaction to the benzyltellurocyanate: the dibenzylthiotelluride was obtained in 90 % yield.

More recently, Nakhdjavan and Klar (128) synthesised tellurium(IV) thiolates and dithiolates from the reaction of tellurium tetrachloride with thiols and dithiols at low temperature. Transesterification reactions between diorganotellurium dialkoxides

and thiols or dithiols have, however, been reported unsuccessful (129).

RESULTS AND DISCUSSION

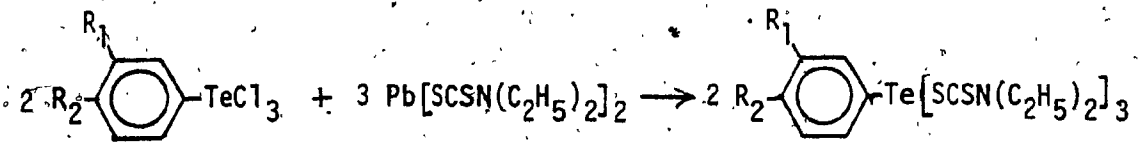
Using lead(II) diethyldithiocarbamate

Lead bis(diethyldithiocarbamate) reacts with tellurium tetrachloride and monoaryltellurium trichlorides in appropriate proportions to give corresponding tellurium(IV) diethyldithiocarbamates in good yields. The representative reactions are noted below:

$$TeCl_4 + n\,Pb[SCSN(C_2H_5)_2]_2 \longrightarrow Cl_{4-n}Te[SCSN(C_2H_5)_2]_n + n\,PbCl_2$$

(n = 1 or 2)

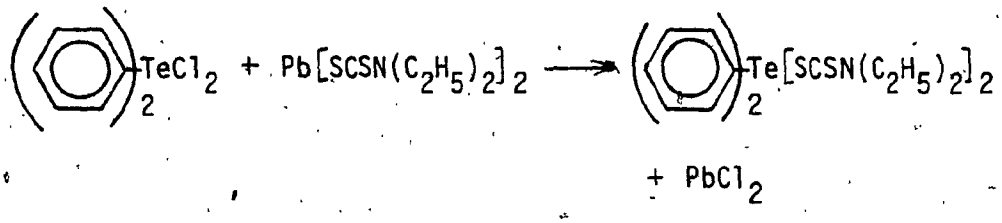
(II-B-3)



$$2\,R_1R_2C_6H_3TeCl_3 + 3\,Pb[SCSN(C_2H_5)_2]_2 \longrightarrow 2\,R_1R_2C_6H_3Te[SCSN(C_2H_5)_2]_3 + 3\,PbCl_2$$

($R_1 = R_2 = H$; $R_1 = H$, $R_2 = CH_3O$; $R_1 = H$, $R_2 = C_2H_5O$; $R_1 = CH_3$, $R_2 = CH_3O$; $R_1 = R_2 = CH_3O$)

(II-B-4)



(II-B-5)

The reaction between diphenyltellurium dichloride and lead bis(diethyldithiocarbamate) did not go to completion even on prolonged stirring under refux. Diphenyltellurium bis(diethyldithiocarbamate) was obtained in low yield.

Attempts to prepare aryltellurium(IV) diethyldithiocarbamates from the reaction of bis(thiocarbamyl)disulfide with diaryltellurides (aryl = phenyl- and 4-methoxyphenyl-) in carbon tetrachloride, chloroform or toluene were unsuccessful: at room temperature, the reactants were recovered unreacted, while under reflux the reaction mixture yielded decomposition products which were not identified.

All the compounds are stable at room temperature and are soluble in common organic solvents. The 270 MHz ^1H nmr spectra of phenyl-, 4-methoxyphenyl-, 4-ethoxyphenyl-, and 3-methyl,4-methoxyphenyl-tellurium tris(diethyldithiocarbamates) in deuteriochloroform are reproduced in Figures II-B-1 to II-B-4 and the chemical shifts are presented in Table II-B-1.

Table II-B-1

^{1}H nmr chemical shifts of monoaryltellurium(IV) dithiocarbamates[a]

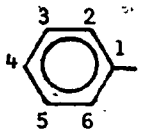
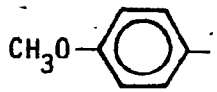
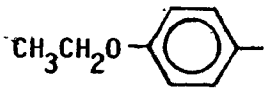
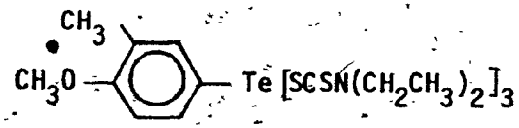
Compound	Chemical Shift δ (ppm)	Assignment
 $Te[SCSN(CH_2CH_3)_2]_3$	8.66	Aryl protons H-3,5
	7.38	Aryl protons H-2,4,6
	3.769	$N-CH_2CH_3$
	1.294	$N-CH_2\underline{CH_3}$
 $Te[SCSN(CH_2CH_3)_2]_3$	8.56	Aryl protons H-2,6
	6.88	Aryl protons H-3,5
	3.796[b]	$N-CH_2CH_3$ + $Ar-O\underline{CH_3}$
	1.297	$N-CH_2\underline{CH_3}$
 $Te[SCSN(CH_2CH_3)_2]_3$	8.55	Aryl protons H-3,5
	6.86	Aryl protons H-2,6
	4.022	$Ar-O\underline{CH_2}CH_3$
	3.772	$N-CH_2\underline{CH_3}$
	1.391	$Ar-O\underline{CH_2}\underline{CH_3}$
	1.295	$N-CH_2\underline{CH_3}$

Table II-B-1 (Contd.)



8.496	Aryl proton H-6
8.352	Aryl proton H-2
6.803	Aryl proton H-5
3.771[c]	$N\text{-}\underline{CH_2}CH_3$ + $Ar\text{-}O\underline{CH_3}$
2.206	$Ar\text{-}\underline{CH_3}$
1.303	$N\text{-}CH_2\underline{CH_3}$

[a] Tetramethylsilane was used as internal standard. Spectra determined at 270 MHz, 0.05M solutions in $CDCl_3$.

[b] Broad signal with no fine structure.

[c] Broadened quartet.

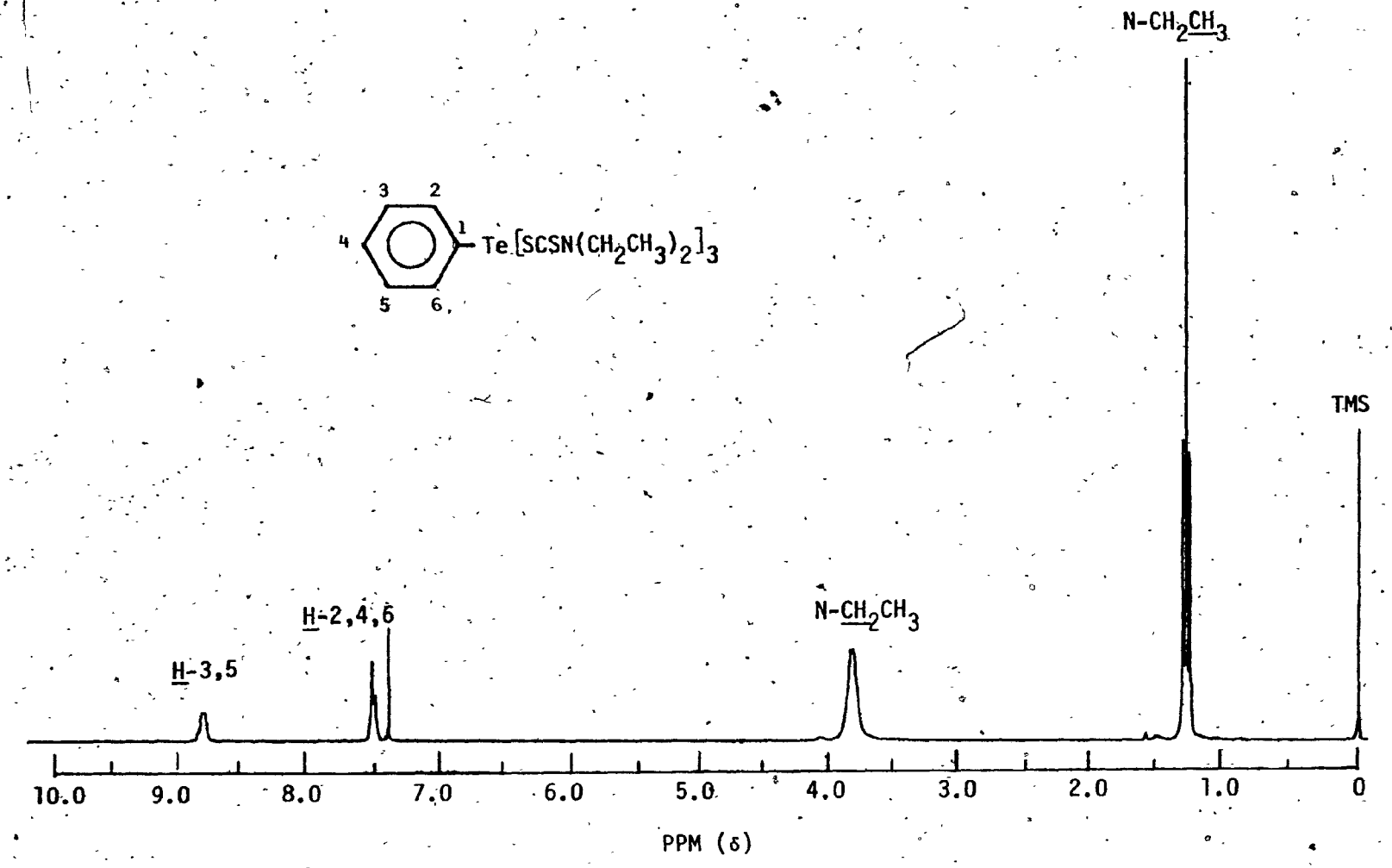


Figure II-B-1: ^1H nmr spectrum of $PhTe[SCSN(C_2H_5)_2]_3$.

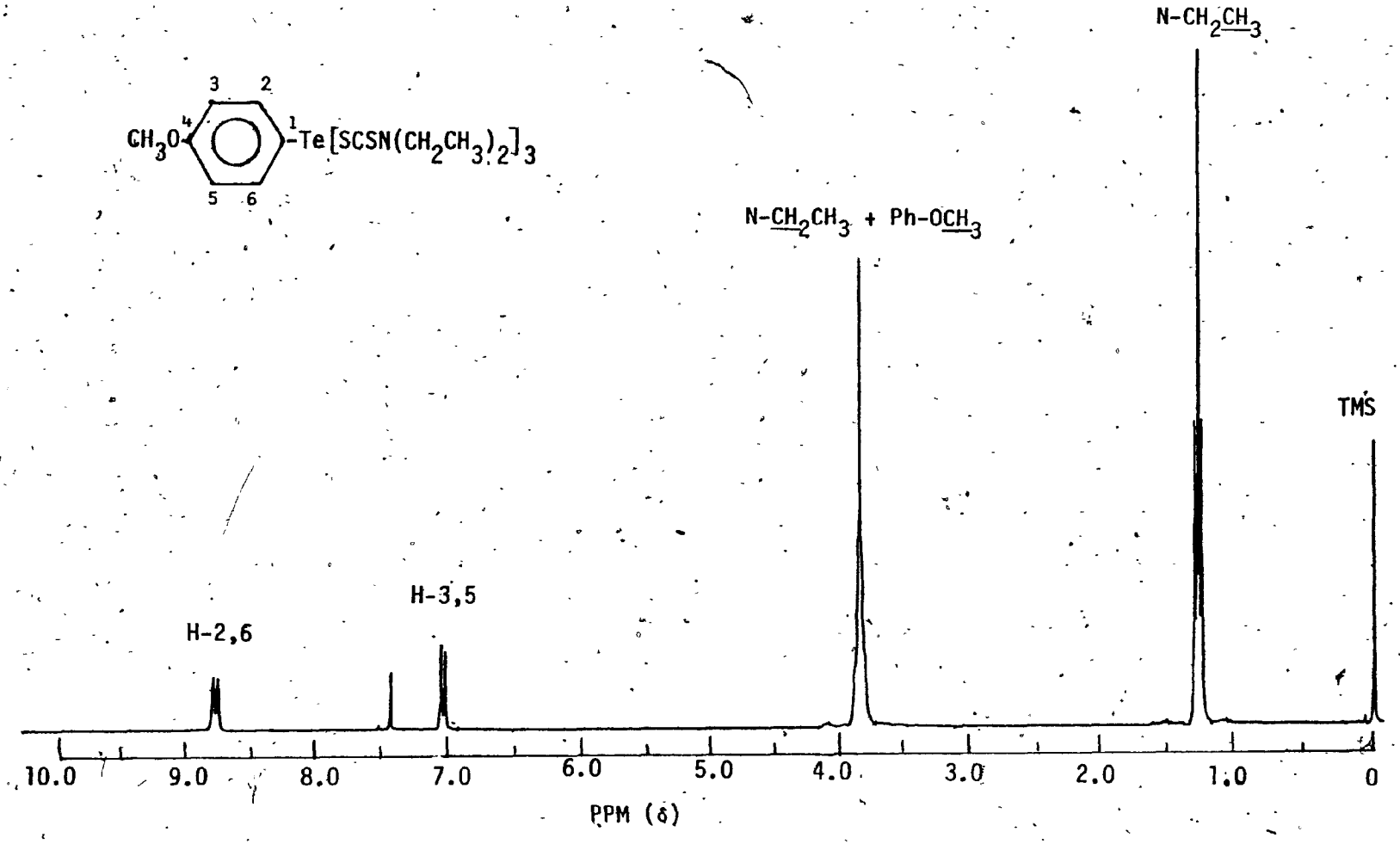


Figure II-B-2: ^1H nmr spectrum of (4-CH_3OPh)Te[SCSN$(C_2H_5)_2]_3$.

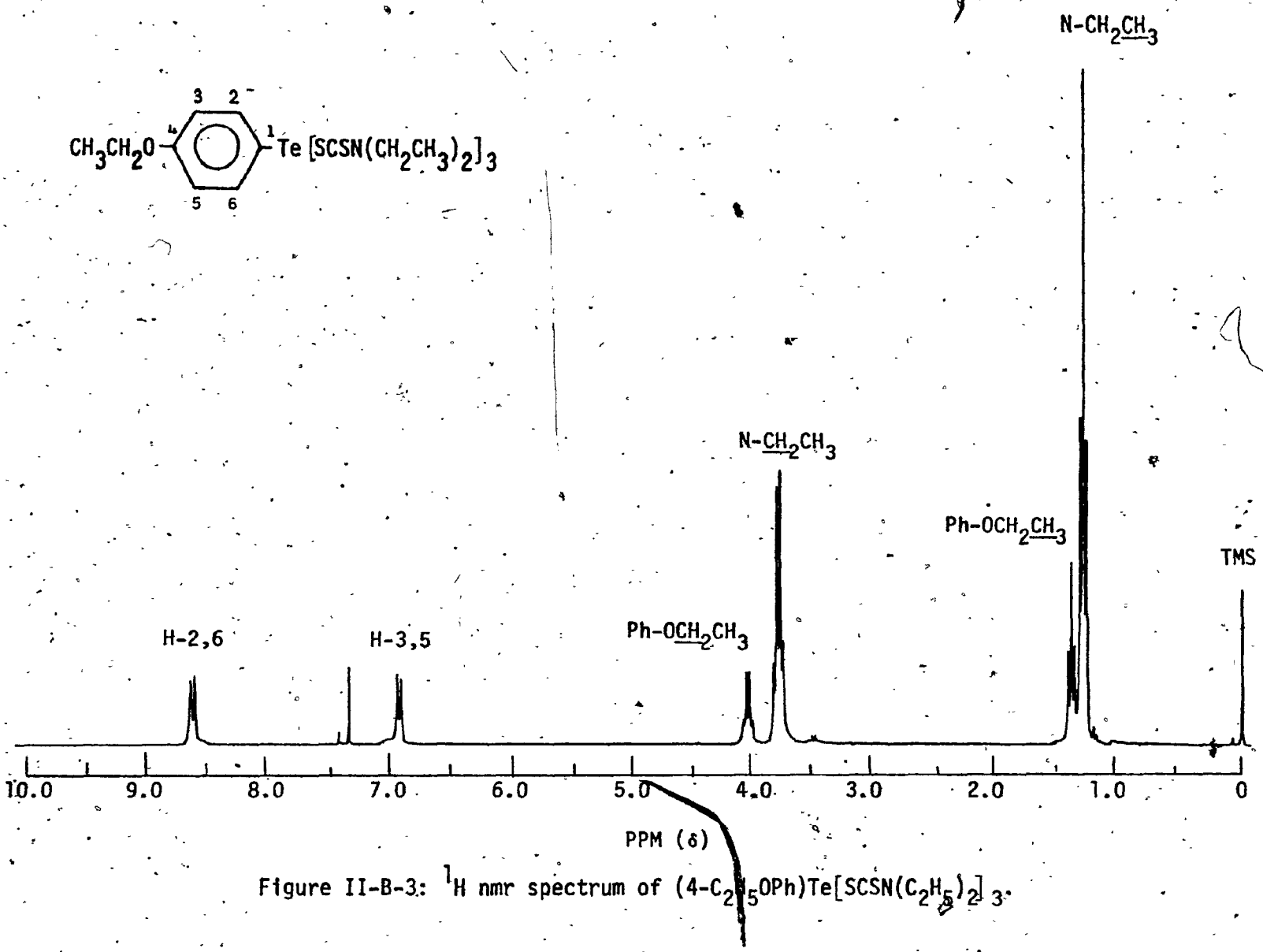


Figure II-B-3: ^1H nmr spectrum of $(4\text{-}C_2H_5OPh)Te[SCSN(C_2H_5)_2]_3$.

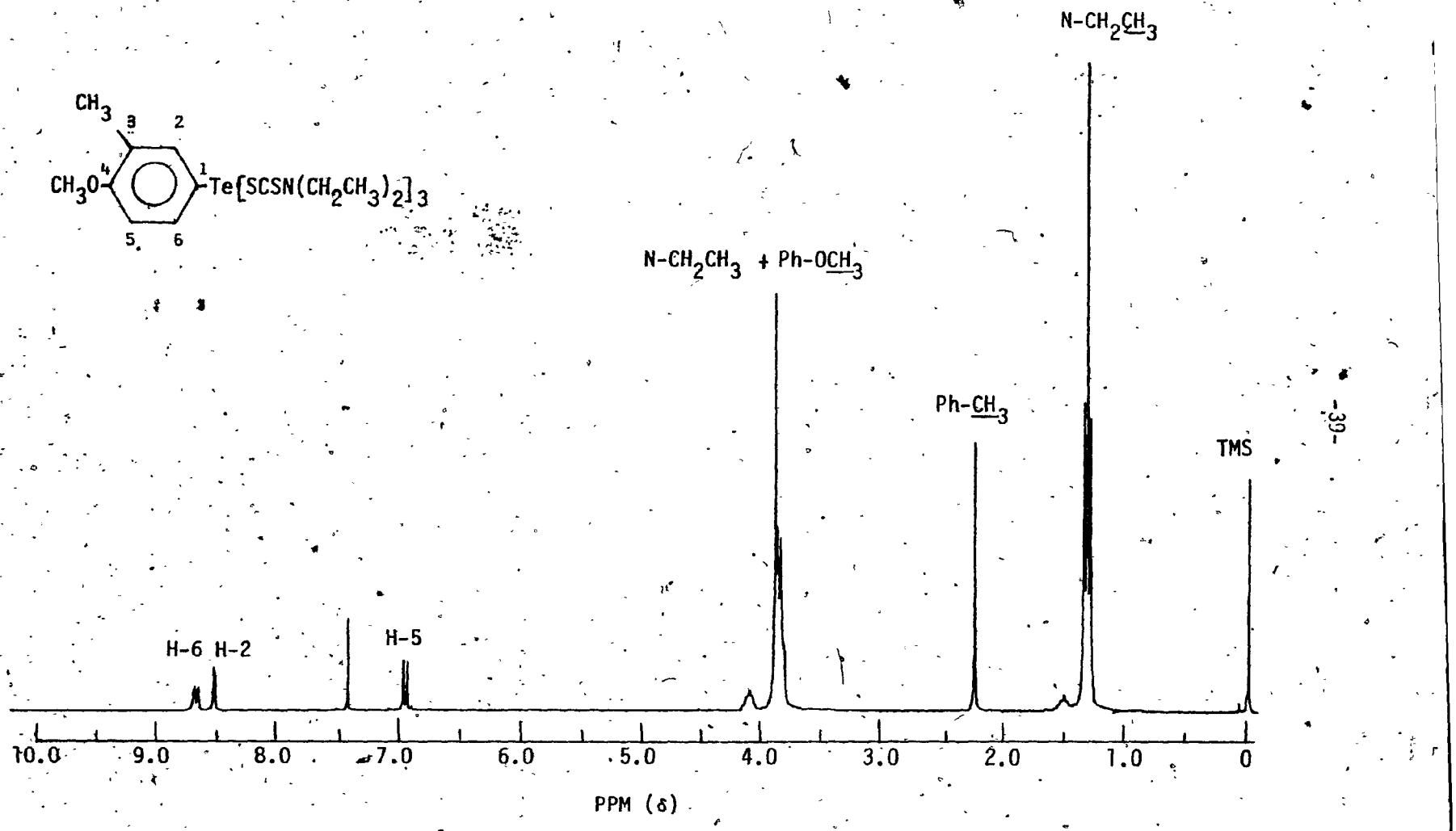
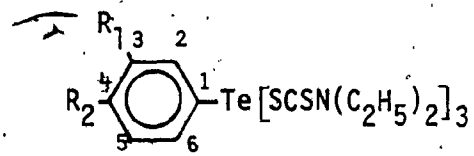


Figure II-B-4: ^1H nmr spectrum of (3-CH_3-4-CH_3OPh)Te[SCSN(C_2H_5)$_2$]$_3$.

Carbon-13 spectra

Carbon-13 chemical shift assignments of the following four monoaryltellurium(IV) dithiocarbamates are collected in Table II-B-2 and are based on a comparison with the sodium salt of diethyldithiocarbamic acid as well as on estimates of the effects of substituents on the aryl moiety, and on considerations of peak intensities. The typical spectra of 4-methoxyphenyltellurium tris(diethyldithiocarbamate) and 4-ethoxyphenyltellurium tris(diethyldithiocarbamate) are illustrated in Figure II-B-5 and II-B-6.



$R_1 = H$, $R_2 = H$.

$R_1 = H$, $R_2 = CH_3O$.

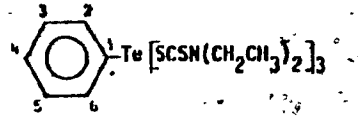
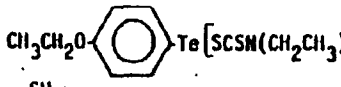
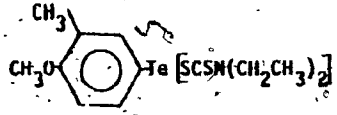
$R_1 = H$, $R_2 = C_2H_5O$.

$R_1 = CH_3$, $R_2 = CH_3O$.

The carbon atoms directly bound to tellurium in the four compounds show chemical shifts within the range 129.5-140.5 ppm. In the phenyltellurium derivative, with no further substitution on the aryl group, the chemical shift of C-1 is 140.5 ppm in $CDCl_3$ solution, 12.0 ppm downfield of benzene. The chemical shift for C-1 in

Table II-B-2

Carbon-13 chemical shifts of monoaryltellurium tris(diethyldithiocarbamates) and solvent effects[a]

Compound	Solvent	1	2	3	4	5	6	CH_3Ph	CH_3OPh	CH_3CH_2OPh CH_2	CH_3CH_2OPh CH_3	C=S	NCH_2CH_3 CH_2	NCH_2CH_3 CH_3
	$CDCl_3$	140.50	133.21	129.10	130.01	129.10	133.21					b	49.91	12.25
	DMSO-d_6	139.92	132.82	128.98	130.01	128.98	132.82					b	49.67	11.91
		+0.58	+0.39	+0.12	0.00	+0.12	+0.39						+0.24	+0.34
	$CDCl_3$	130.17	135.30	114.58	160.92	114.58	135.30		55.35			198.95	49.85	12.30
	DMSO-d_6	b	134.92	114.51	161.54	114.51	134.92		55.24			196.80	49.52	11.89
			+0.38	+0.07	-0.62	+0.07	+0.38		+0.11			+2.15	+0.33	+0.41
	$CHCl_3$	130.67	135.52	115.16	160.69	115.16	135.52			64.06	15.35	199.07	50.54	12.56
	DMSO	129.49	134.89	115.20	162.32	115.20	134.89			65.51	14.60	197.56	49.98	11.81
		+0.18	+0.63	-0.04	-1.63	-0.04	+0.63					+1.51	+0.56	+0.75
	$CDCl_3$	130.10	135.60	127.30	159.70	110.45	132.88	16.42	55.60			198.48	49.50	12.25
$NaSCSN(CH_2CH_3)_2$[c]	D_2O											206.4	49.5	12.36

a PPM from TMS; b Not observed; c ref. (130).

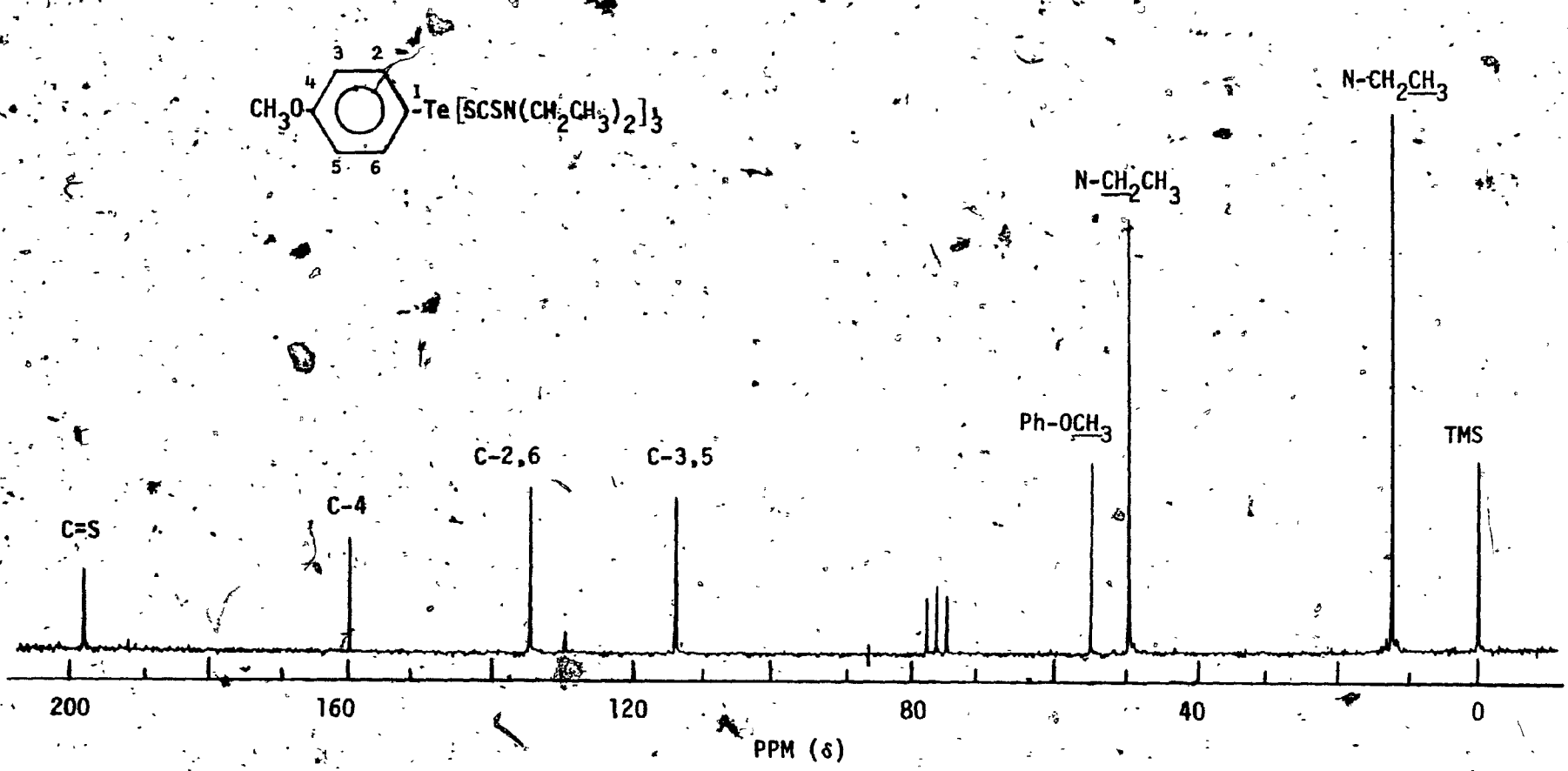


Figure II-B-5: ^{13}C spectrum of (4-CH_3OPh)Te[$SCSN(C_2H_5)_2$]$_3$

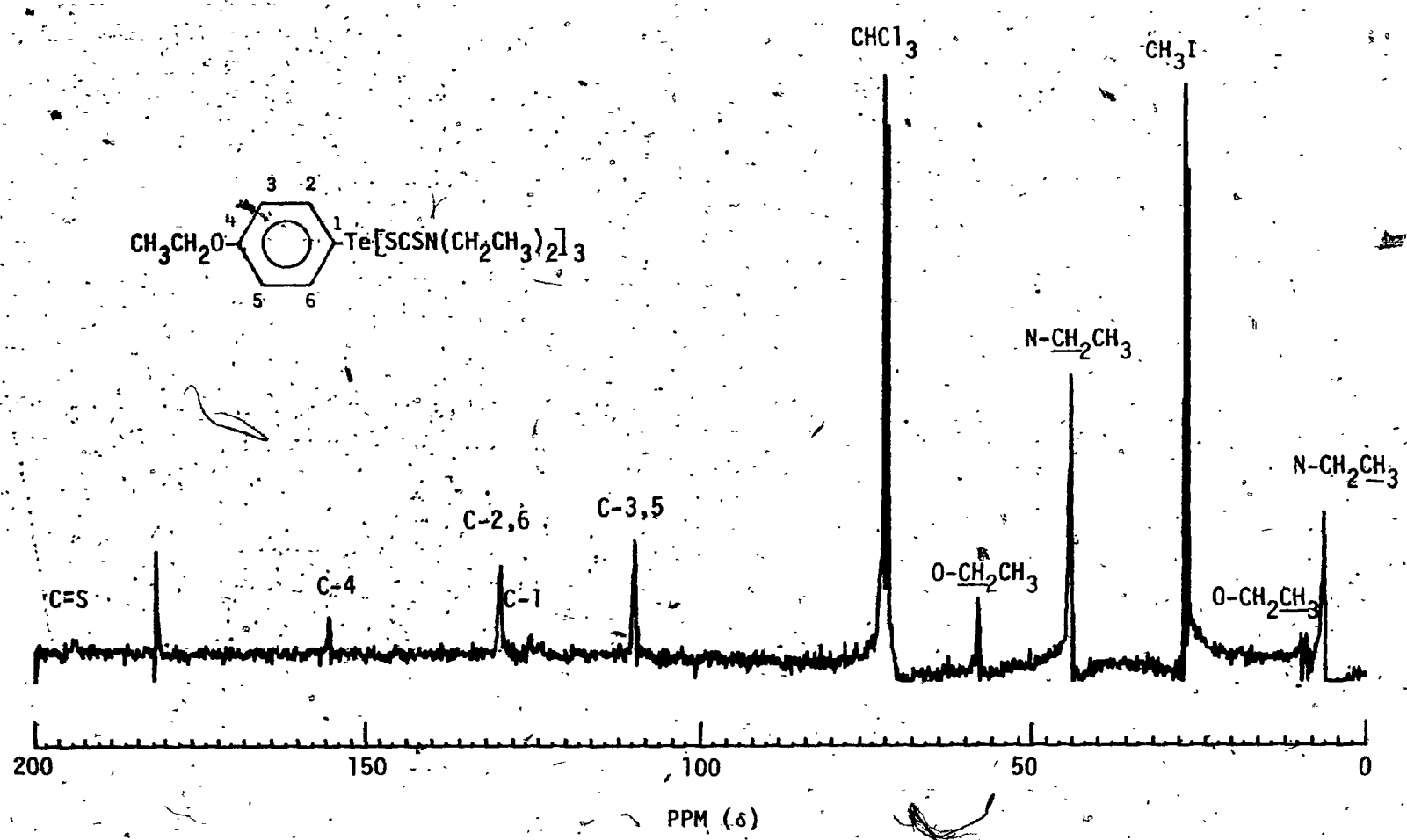


Figure II-B-6: ^{13}C nmr spectrum of $(4\text{-}C_2H_5OPh)Te[SCSN(C_2H_5)_2]_3$

diphenylditelluride has been reported (131-133) at 108.0 ppm, and in methylphenyltelluride (134,135) at 112.5-112.6 ppm, i.e. 16-20 ppm upfield from benzene. In these cases, each tellurium atom has available two lone-pairs of electrons that may affect the electron density over the carbon atom directly attached to tellurium. Llabres et. al. (135) have examined the ^{13}C shielding of anisole analogues (CH_3-Y-Ph; Y = O, S, Se and Te), and suggested that a "heavy atom effect" must be invoked for the interpretation of the methyl and the aryl carbon shielding in the tellurium compounds. They did not elaborate on what this "heavy atom effect" might be. The presence of polar Te-S bonds, with their inductive influence, together with the availability of only one lone pair of electrons on the tellurium atom, would be expected to significantly modify the effect of the tellurium atom on C-1, so that the observed substantial deshielding of C-1 carbon atoms in the other tellurium compounds (131,134,135) is not surprising.

At 129.1 ppm, the chemical shift of the meta carbon atoms is very similar to that of benzene (128.5 ppm), phenylmethyltelluride (128.7-129.0) (134,135), and diphenylditelluride (129.2-129.3) (131-133) indicating a very small inductive effect of the -Te(diethyldithiocarbamate)$_3$ group, the displacement of the para carbon signal at 130.0 ppm is in the same deshielding direction as that of C-1 carbon (i.e. the -Te(diethyldithiocarbamate)$_3$ group reduces the charge density). In contrast, the para carbon signal is displaced in the shielding direction (as is the C-1 signal) in

phenylmethyltelluride (at 126.6-127.1 ppm) (134,135), and in diphenyditelluride (at 128.0-128.1 ppm) (131-133). The ortho carbon atoms in phenyltellurium tris(diethyldithiocarbamate) are somewhat shielded compared to the corresponding carbons in methylphenyltelluride (136.2-136.7 ppm) (134,135) and in diphenylditelluride (137.6-137.7 ppm) (131-133).

Transfer of electron density between the lone-pair of electrons on tellurium and the aryl group is expected to be influenced by changes in the degree of polarization of the adjacent sulfur-carbon bonds, the effect operating through the covalent or coordinate Te-S bonds. Consequently, the chemical shift of C-1 is expected to be solvent dependent. Shielding of C-1 by 0.58 in the phenyltellurium tris(diethyldithiocarbamate) and by 0.18 ppm in 4-ethoxyphenyltellurium derivative in DMSO compared to $CDCl_3$ has, indeed, been observed. Table II-B-2, which summarizes the solvent effects of the ^{13}C chemical shifts, shows that, in fact all of the carbon atoms in those compounds, except C-4 in 4-methoxyphenyl- and 4-ethoxyphenyl-tellurium tris(diethyldithiocarbamate) compounds, are shielded in DMSO as compared to $CDCl_3$, or are unaffected.

Thiocarbonyl carbons absorb over the range 180-210 ppm (136), while in the structurally related sodium diethyldithiocarbamate the thiocarbonyl carbon absorbs (130) at 206.4 ppm in D_2O solution. The thiocarbonyl carbons in the compounds under investigation absorb within the narrow range 197.5-199.1 ppm.

Evidently, variations in the effects of substituents on the aryl moiety have little effect on the relatively remote thiocarbonyl carbon atoms. The three thiocarbonyl carbon atoms give rise to relatively weak signals. In phenyltellurium tris(diethyldithiocarbamate), the ^{13}C thiocarbonyl signal in 0.1 M $CDCl_3$ or DMSO-d_6 solutions could not be observed, even though 35,000 transient scans were taken. Although the thiocarbonyl carbon signal of 4-methoxyphenyltellurium tris(diethyldithiocarbamate) in $CDCl_3$ is sharp, and easily observable after 5,000 transients, over 60,000 transients were required for this signal to be detectable in DMSO-d_6 solution. It then shows considerable broadening.

The observation of shielding (2.15 or 1.51 ppm, respectively) of the thiocarbonyl carbon atoms of 4-methoxyphenyl- and 4-ethoxyphenyltellurium tris(diethyldithiocarbamate) in DMSO (or DMSO-d_6) compared to $CHCl_3$ (or $CDCl_3$) solutions (Table II-B-2) suggests specific solvation of the thiocarbonyl group by the polar solvent. A similar pattern has been observed in 3-N-aryl-1(H)-2-thioxo-4-imidazolidinones (137), where the thiocarbonyl carbons are shielded by about 1.9 ppm in DMSO as compared with $CHCl_3$.

The C-4 carbon atoms in 4-methoxyphenyl- and 4-ethoxyphenyltellurium tris(diethyldithiocarbamate) are deshielded (by 0.62-1.63 ppm) in DMSO compared to chloroform, indicating specific solvation on the ether oxygen atom. In contrast, the chemical shift of C-4 in the unsubstituted phenyltellurium tris(diethyldithiocarbamate) is unaffected by this change in solvents.

Stereochemical considerations

In recent years, several reports have appeared on kinetic studies of transition metal dithiocarbamate complexes (138-140). Two kinetic processes which can influence the nmr spectra of metal dithiocarbamate complexes have been proposed: (1) metal-centered rearrangement, and (2) $S_2C{=}N$ bond rotation. In the present study, a clear distinction between the two processes could not be made, but, for reasons described below; type 1 appears to be more probable.

The X-ray crystal structure determination (53,54) of phenyltellurium tris(diethyldithiocarbamate) shows that the diethyldithiocarbamate ligands occupy two enantiotopically and one diastereotopically related sites (Figure II-B-7). Thus, the stereochemistry of bidentate ligands is such that considerable multiplicity of both the ^{13}C and the ^{1}H spectra would be expected if the solution and the solid state structures were similar, and if the solution species were conformationally stable.

Both the ^{13}C and the ^{1}H nmr spectra (Figures II-B-1 to II-B-6) of all the compounds in the series are quite inconsistent with the solid state structure of phenyltellurium tris(diethyldithiocarbamate) and are, in fact, typical of species undergoing a rapid exchange process. The 270 MHz ^{1}H spectra show the number of signals expected for an exchanging system, and show

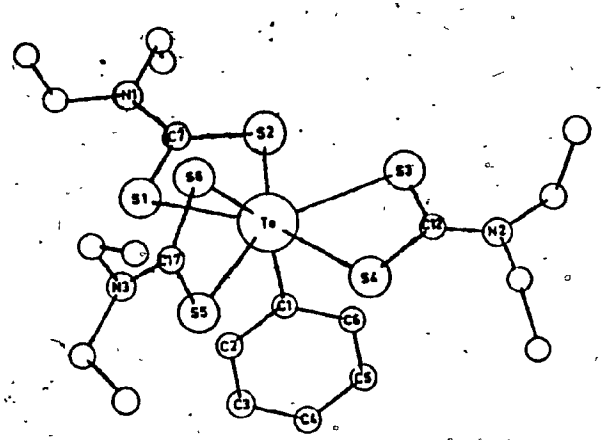


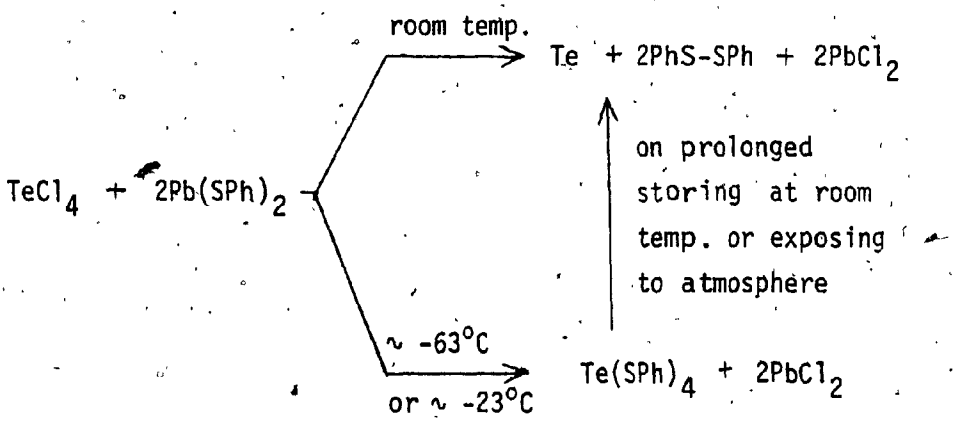
Figure II-B-7: Crystal structure of $PhTe(SCSN(C_2H_5)_2)_3$

detectable broadening at the probe temperature of 23°C for the N-methylene signals only; in the case of 4-ethoxyphenyltellurium tris(diethyldithiocarbamate) almost no broadening is visible. Except as noted above, the ^{13}C spectra also show the minimum expected number of sharp signals.

A metal-centered exchange process involving two stereochemically distinct sites is consistent with the failure to observe the thiocarbonyl ^{13}C signal for phenyltellurium tris(diethyldithiocarbamate). The proton spectra of phenyl-, 4-methoxyphenyl-, and 3-methyl-4-methoxyphenyl-tellurium tris(diethyldithiocarbamates) show incomplete time-averaging of the N-methylene signals. The case of the 4-methoxyphenyltellurium derivative is especially interesting, since the $CDCl_3$ solution shows the sharp, easily observable thiocarbonyl signal expected for a system undergoing fast metal-centered exchange process. In contrast, the corresponding signal of DMSO-d_6 solutions can be observed only with difficulty because of its low intensity, and has the appearance typical of exchange broadening. These data suggest that the rate of ligand-centered exchange is slower in DMSO-d_6 than in $CDCl_3$ solution. Fast $S_2C = N$ bond rotation is a less likely exchange process since it should not average the ^{13}C thiocarbonyl signals in the two stereochemically distinguishable types of ligands.

Using lead(II) benzenethiolate

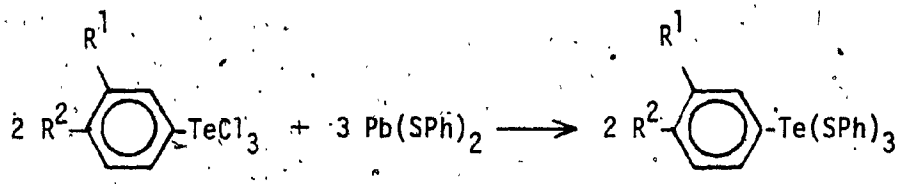
Lead bis(benzenethiolate) when treated with tellurium tetrachloride or monoaryltellurium trichlorides at room temperature gave decomposition products. The synthesis of tellurium tetrakis(benzenethiolate) could only be achieved at ∿-63°C. When tellurium tetrachloride and lead bis(benzenethiolate) were reacted in a 1:2 molar ratio at ∿-23°C and the temperature was allowed to increase slowly to room temperature, the reaction produced a mixture of both biphenyldisulfide and the desired tellurium tetrakis(benzenethiolate). At room temperature, the reaction, however, gave biphenyldisulfide exclusively.



Although an attempt to prepare dichlorotellurium bis(benzenethiolate) was successful at low temperature, during work up it decomposed into biphenyldisulfide and tellurium dichloride. In air the latter

disproportionated into tellurium tetrachloride and elemental tellurium as was also reported by Aynsely (141).

The synthesis of monoaryltellurium tris(benzenethiolate) compounds has been achieved according to reaction II-B-6.



$$2\ R^2\text{-}C_6H_3(R^1)\text{-}TeCl_3 + 3\ Pb(SPh)_2 \longrightarrow 2\ R^2\text{-}C_6H_3(R^1)\text{-}Te(SPh)_3 + 3\ PbCl_2$$

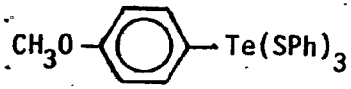
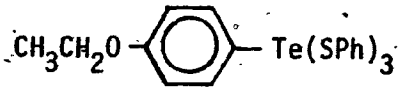
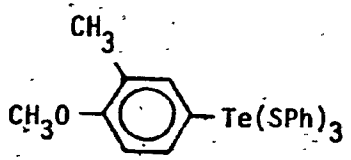
$(R^1 = H,\ R^2 = CH_3O;\ R^1 = H;\ R^2 = C_2H_5O;\ R^1 = CH_3,\ R^2 = CH_3O)$

(II-B-6)

The proton chemical shifts of the three compounds are given in Table II-B-3 and the spectra are reproduced in Figures II-B-8 to II-B-10. All the compounds are thermally unstable and sensitive to atmospheric oxygen and moisture. They are soluble in almost all organic solvents. The solid and the solution of 4-methoxyphenyltellurium tris(benzenethiolate) decompose readily on exposure to air and on standing at room temperature for a day or two. The corresponding 4-ethoxyphenyltellurium- and 3-methyl-4-methoxyphenyltellurium derivatives decomposed only on prolonged storing.

Table II-B-3

^{1}H nmr chemical shifts of monoaryltellurium tris(benzenethiolates)

Compound	Chemical shift δ (ppm)[a]	Multiplicity[b]/ Assignment
	8.16-7.33 (7.44) 6.92 3.83	m; -SPh d; CH_3OPh- s; $\underline{CH_3}OPh$
	8.06-7.23 (7.64) 6.85 4.14 1.43	m; -SPh d; CH_3CH_2OPh- q; $CH_3\underline{CH_2}OPh$- t; $\underline{CH_3}CH_2OPh$
	7.90-6.96 (7.43) 6.73 3.76 2.16	m; -SPh d; CH_3CH_2OPh- s; $CH_3OPh(\underline{CH_3})$- s; $\underline{CH_3}OPh(CH_3)$-

[a] Center of the peak.

[b] s = singlet, d= doublet, t = triplet, q = quartet.

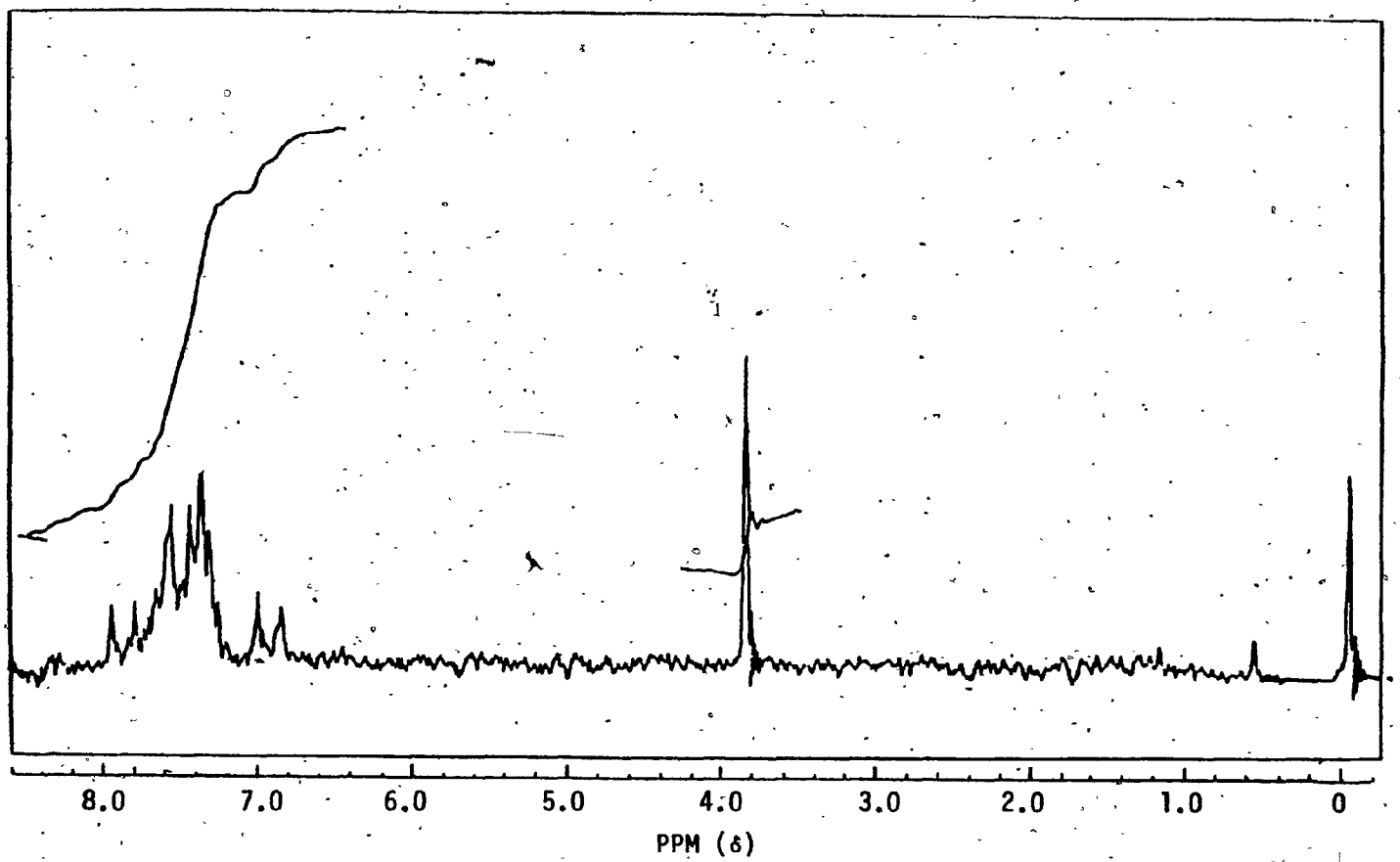


Figure II-B-8: ^1H nmr spectrum of $(4\text{-}CH_3OPh)Te(SPh)_3$

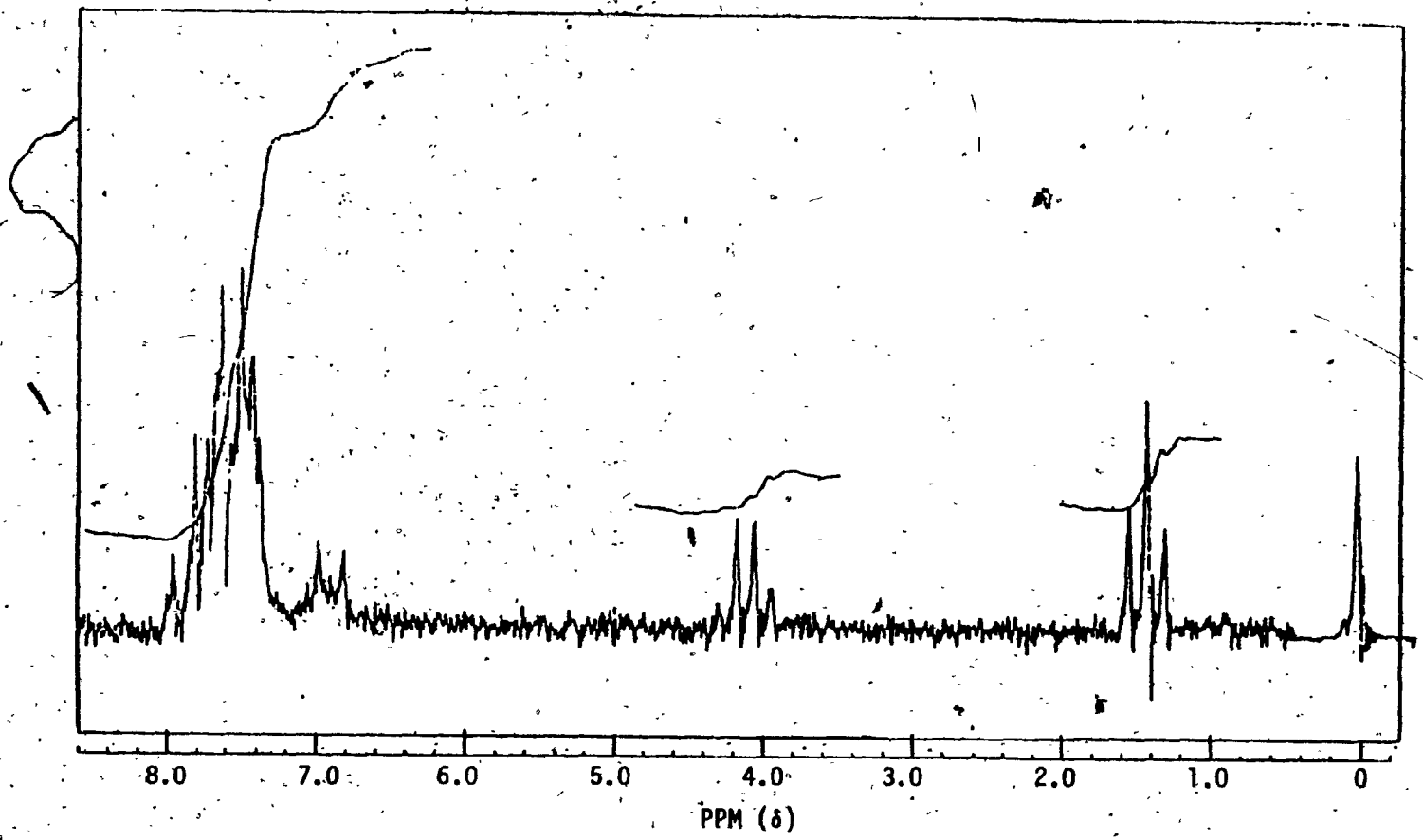


Figure II-B-9: ^1H nmr spectrum of $(4\text{-}C_2H_5OPh)Te(SPh)_3$

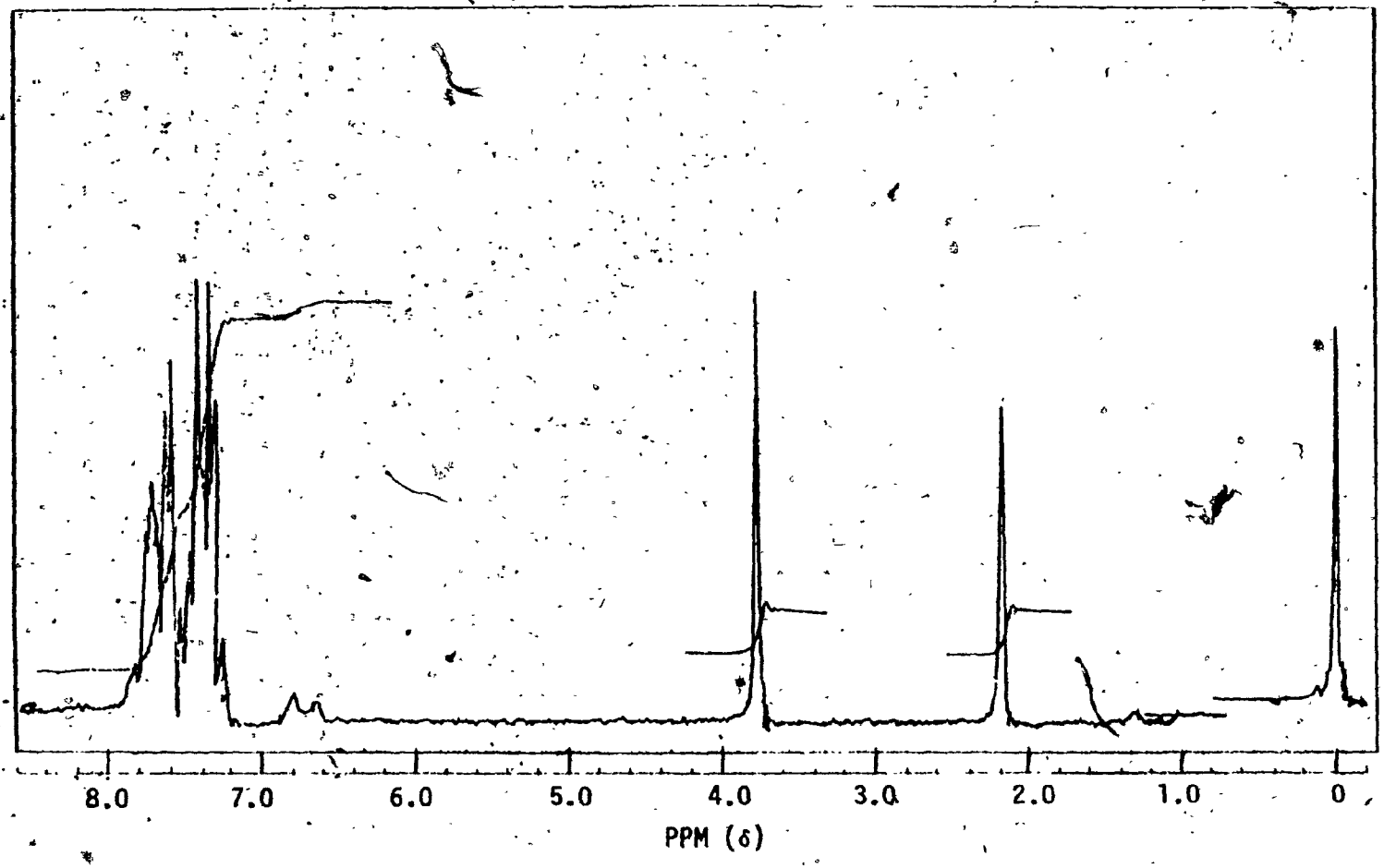


Figure-II-B-10: ^{1}H nmr spectrum of $(3\text{-}CH_3\text{-}4\text{-}CH_3OPh)Te(SPh)_3$

The reactions involved triphenyllead benzenethiolate as the reagent did not produce the desired tellurium benzenethiolate derivatives. With diphenyltellurium dichloride, a mixture of diphenyltelluride, biphenyldisulfide and triphenyllead chloride is obtained. Though the mechanism of this reaction could not be established with certainty, it is proposed that the reaction initially produces diphenyltellurium bis(benzenethiolate) which subsequently disproportionates, under the reaction conditions, into diphenyltelluride and biphenyldisulfide. The equation for the reaction may be written as below:

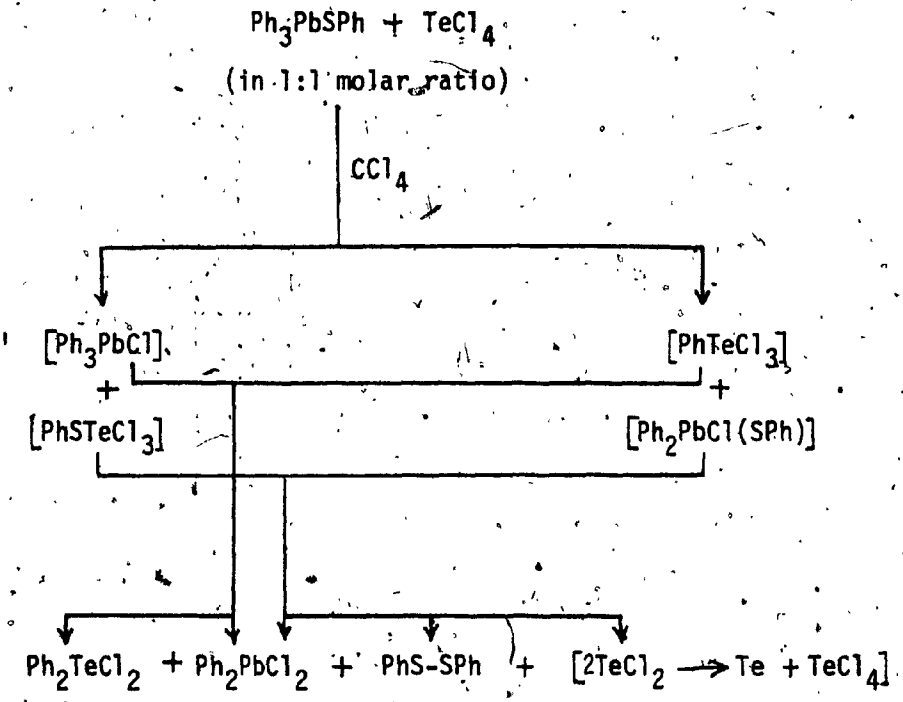
$$Ph_2TeCl_2 + 2\ Ph_3Pb(SPh) \longrightarrow 2\ Ph_3PbCl + [Ph_2Te(SPh)_2] \downarrow$$

$$Ph_2Te + PhS\text{-}SPh$$

(II-B-7)

The reaction between tellurium tetrachloride and triphenyllead benzenethiolate was found to be very complex. Irrespective of the way of mixing the two reactants, the reaction produced a mixture of diphenyltellurium dichloride, diphenyllead dichloride, biphenyldisulfide and elemental tellurium. On the basis of thin-layer chromatography results and the amounts of the components

isolated, it is proposed that the reaction proceeds according to scheme II-B-8:



(II-B-8)

Evidently, the complexity in the reaction arises from the simultaneous cleavage of Pb-C(aryl) and Pb-S bonds in triphenyllead benzenethiolate.

SECTION C: EXPERIMENTAL

GENERAL TECHNIQUES

The chemicals listed in Table II-C-1 were obtained commercially and for the most part, were used without further purification. The solvents, diethylether, petroleum-ether (40-60°), hexane and tetrahydrofuran were dried by refluxing over sodium for two days. In the case of halogenated solvents, anhydrous calcium chloride was used as a drying agent. Absolute methanol and ethanol were prepared according to the method of Lend and Djerrium (142) by refluxing over magnesium and iodine (10:1) for two hours. All the solvents were distilled before use.

The syntheses of certain chemicals, which were not commercially available to the author, were achieved according to reported methods. Various reactions used in the preparation are summarized in Table II-C-2.

Lead bis(benzenethiolate) was synthesised following the reported method (150) by treating benzenethiol with lead(II) acetate in absolute ethanol. The yellow product was washed with hot water and finally dried under vacuum. The lead salt of diethyldithiocarbamic acid was prepared from the reaction of sodium diethyldithiocarbamate with lead(II) acetate in water (151).

Table II-C-1

Source of chemicals and solvents

Chemicals	
Anisole	Fisher Scientific Co.
Bromobenzene	Fisher Scientific Co.
Lead dichloride	Anachemia Ltd.
Methyliodide	Fisher Scientific Co.
2-Methylanisole	Fisher Scientific Co.
2-Methoxyanisole	Fisher Scientific Co.
Magnesium metal fillings (Grignard)	Anachemia Ltd.
Phenetole	Fisher Scientific Co.
Phenylboric acid	Raylo Chemicals Ltd.
Sodium diethyldithiocarbamate	Fisher Scientific Co.
Sodium sulfate (anhydrous)	Anachemia Ltd.
Tellurium tetrachloride	Alfa Products Inc.
Thallous chloride	Fisher Scientific Co.
Benzenethiol	Aldrich Chemicals Co.
Solvents	
Acetic acid (glacial)	Van Water Chemicals
Benzene (reagent)	Anachemia Ltd.
Chloroform (N.F.)	Fisher Scientific Co.
Carbon tetrachloride	Anachemia Ltd.
Diethylether	Anachemia Ltd.
Dichloromethane	Anachemia Ltd.

Hexane	Anachemia Ltd.
Tetrahydrofuran (certified)	Fisher Scientific Co.
Toluene	Eastman Kodak Co. Ltd.

Table II-C-2

Various reactions, compounds isolated and their melting points

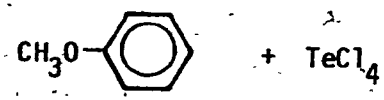
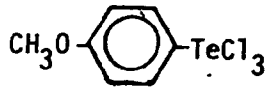
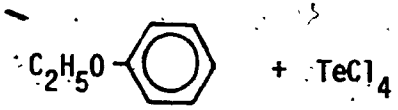
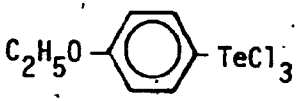
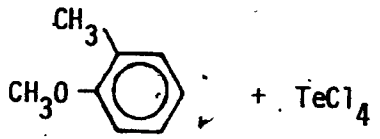
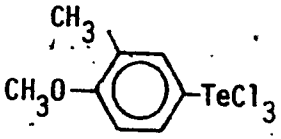
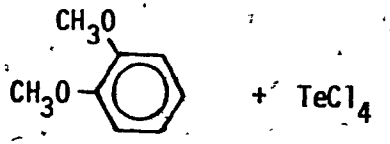
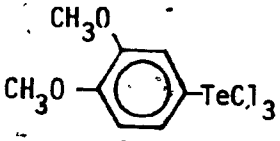
Reaction	Compound Isolated	M.P. (°C) (lit. value)	Reference(s)
		189-190 (190)	80
		185 (185)	81
		231 (232-233)	89
		180-181 (181)	89
2PhMgBr + $PbCl_2$[a]	Ph_4Pb	226-229 (228)	143,144

Table II-C-2 (Contd.)

$2RMgBr + PbCl_2$	Ph_6Pb_2	154-156 155	143
R = (Methyl-; phenyl-; p-tolyl-)	$(p\text{-tolyl})_6Pb_2$	194-195 (193)	145
	Me_6Pb_2	36-38 (38)	146
$MeMgI + PbCl_2$[b]	Me_4Pb[c]	-	147
$Ph_4Pb + (NH_4)_2PbCl_6$	Ph_3PbCl	207 (208)	148
$Ph_3PbCl + Pb(SPh)_2$	$Ph_3Pb(SPh)$	106 (106-107)	149
$2PhB(OH)_2 + TlCl_3$	Ph_2TlCl	>310 (>310)	114
$PhB(OH)_2 + TlCl_3$	$PhTlCl_2$	235 (dec.) (235 (dec.))	114

[a] $2RMgBr + PbCl_2 \longrightarrow [R_2Pb] + 2MgCl_2$

$2[R_2Pb] \longrightarrow R_4Pb$

$2[R_2Pb] \longrightarrow R_6Pb_2 + Pb$

[b] The reaction was carried out in the presence of methyliodide.

[c] Used ethereal solution.

All the reactions were carried out in a two or three-necked round bottom flask, equipped with nitrogen gas inlet and outlet tubes, a reflux condenser and if necessary a tube to add solid reactants, or a pressure-equalizing dropping funnel. The reactions were usually monitored by thin-layer chromatography on plates precoated with silica-gel. A mixture of benzene:acetic acid (9.5:0.5) was used as the solvent, and 0.1 % solution of dithiazone in chloroform as the developer.

Chemical analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennesse, U.S.A., and by Organic Micro-analysis, Montreal, Canada.

Melting points were determined on a Gallenkamp melting point apparatus. The air-sensitive compounds were packed in capillary tubes in a nitrogen-filled glove bag and sealed with modelling clay. The reported melting points are uncorrected.

The proton nmr spectra of all the compounds were measured on a Varian A-60 A spectrometer at room temperature. With a view to studying the exchange behavior of the diethyldithiocarbamate moiety in solution, the ^1H nmr spectra of monoaryltellurium tris(diethyldithiocarbamates) were determined on the 270 MHz "home-built" spectrometer at Chemistry Department, University of British Columbia, Vancouver, B.C., Canada. This was based on a

Bruker WH-90 console, a Nicolet 1080 or 1180 computer and an Oxford Instrument superconducting magnet. Four scans of 0.05 M solutions in deuteriochloroform were taken, using a 16 K word data block.

The noise-decoupled Fourier transform ^{13}C nmr spectra of four monoaryltellurium tris(diethyldithiocarbamates), $RTe(SCSN(CH_2CH_3)_2)_3$ (where R = C_6H_5-, 4-$CH_3OC_6H_5$-, 4-$CH_3CH_2OC_6H_5$-, and 3-CH_3,4-$CH_3OC_6H_4$-), were measured either on an exensively modified Varian HA-100 (25.1 MHz), or on a Bruker WH-90 (22.6 MHz) spectrometer. Spectra were run at probe temperatures of about 35 and 27° on the HA-100 and WH-90, respectively. In all cases, except for the phenyl derivative, approximately 0.5 M solutions were employed; for phenyltellurium tris(diethyldithiocarbamate) the solutions were 0.1 M. The solvents employed were either deuterated or undeuterated chloroform and dimethylsulfoxide. On the modified HA-100 spectrometer when chloroform was used as a solvent, the homonuclear lock signal and the external reference were derived from $^{13}CH_3I$ contained in a capillary; DMSO itself provided the signal as well as the internal reference. Chemical shifts are reported relative to tetramethylsilane (TMS) and were calculated relative to the signals of DMSO and DMSO-d_6 (40.64 and 39.56 ppm, respectively, downfield of TMS). These are estimated to be accurate to ± 0.05 ppm.

REACTIONS WITH ORGANOLEAD(IV) COMPOUNDS

Various reactions, m.p.'s, and yields are summarized in Tables II-C-3 and II-C-4 and the typical experiments are described below:

Reaction between Tellurium tetrachlorde and Tetramethyllead

A toluene (20 ml) solution of tetramethyllead (0.5 g, 2.0 mmol) was added dropwise to a stirred solution of tellurium tetrachloride (0.5 g, 2.0 mmol) in 75 ml of toluene. The reaction mixture was stirred for eight hours and then filtered. On evaporation under vacuum the filtrate gave crude dimethyltellurium dichloride. The product was recrystallized from absolute ethanol and finally dried under vacuum .

Reaction between (4-Ethoxyphenyl)tellurium trichloride and Tetramethyllead

Tetramethyllead (0.8 g, 3.0 mmol) and (4-ethoxyphenyl)tellurium trichloride (0.8 g, 3.0 mmol) were mixed in the same manner as described above. The reaction mixture was stirred overnight and then filtered. The filtrate after distilling away excess solvent gave a white solid which on recrystallization yielded pure methyl(4-ethoxyphenyl)tellurium dichloride.

Table II-C-3

Reactions of tellurium(IV) chloride with tetramethyllead and hexaorganodileads

Reactants (molar ratio)	Diaryltellurium dichloride obtained	M.P. (°C) (lit. value)	Yield %
$TeCl_4$ + $(CH_3)_4Pb$ (1:1)	$(CH_3)_2TeCl_2$	92-94 (92-97)	80
$TeCl_4$ + $(CH_3)_6Pb_2$ (2:1)	$(CH_3)_2TeCl_2$	92-94 (92-97)	78
$TeCl_4$ + Ph_6Pb_2 (2:1)	Ph_2TeCl_2	157-158 (160)	94
$TeCl_4$ + $(H_3C\text{-}C_6H_4)_6Pb_2$ (2:1)	$(H_3C\text{-}C_6H_4)_2TeCl_2$	165-166 (166-167)	86

Table II-C-4

Reactions of monoaryltellurium(IV) chlorides with organoleads

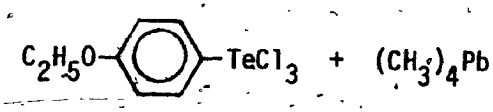
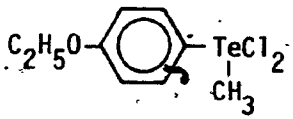
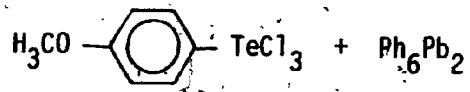
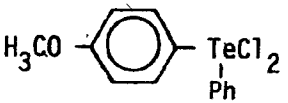
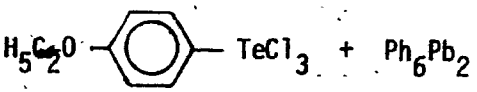
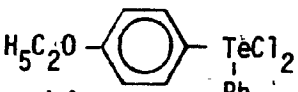
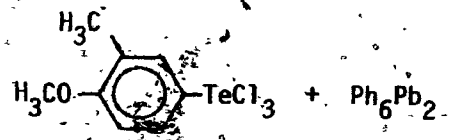
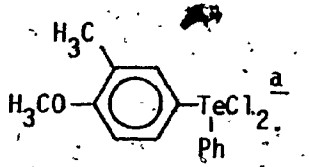
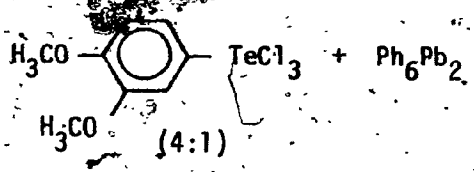
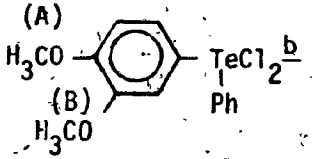
Reactants (molar ratio)	Diorganotellurium dichloride obtained	M.P. (°C) (lit. value)	Yield %
 (1:1)		93-95	95
 (4:1)		113 (114-115)	89
 (4:1)		113-114 (113-115)	92

Table II-C-4 (Contd.)

 (4:1)	 [a]	106-108	78
 (4:1)	 [b]	146-148	73

[a] C 42.25% (found), 42.38% (calcd.), H 3.69% (found), 3.55% (calcd.).

[b] C 40.86% (found, 40.74% (calcd.), H 3.56% (found), 3.41 (calcd.).

Reaction between Tellurium tetrachloride and Hexaphenyldilead (2:1)

To a solution of tellurium tetrachloride (1.1 g, 4.0 mmol) in toluene (125 ml) was added a solution of hexaphenyldilead (1.8 g, 2.0 mmol) in 75 ml of toluene with stirring. An immediate precipitate appeared. The reaction mixture was stirred for four more hours while the reaction was monitored by thin-layer chromatography. Periodic sampling showed the disappearance of hexaphenyldilead and the formation of triphenyllead chloride and diphenyltellurium dichloride. After completion of the reaction (as indicated by the complete disappearance of the spots on the thin-layer chromatographic plates for hexaphenyldilead and triphenyllead chloride), the mixture was filtered. On evaporation under vacuum, the filtrate gave white crystals of diphenyltellurium dichloride. This was recrystallized from absolute methanol.

From the residue left after filtration, lead dichloride and diphenyllead dichloride were isolated and characterized.

Reaction between (4-Ethoxyphenyl)tellurium trichloride and Hexaphenyldilead (4:1)

A solution of hexaphenyldilead (1.8 g, 2.0 mmol) in toluene (100 ml) was mixed dropwise into a suspension of (4-ethoxyphenyl)tellurium trichloride (2.8 g, 8.0 mmol) in the same solvent. After stirring for six hours, the reaction mixture was

filtered and worked up as described above. The crude product, phenyl(4-ethoxyphenyl)tellurium dichloride, was recrystallized from absolute methanol.

REACTION WITH ARYLELEMENT(III) REAGENTS

Various reactions using arylelement(III) compounds as reagent are given in Table II-C-5 and the typical experiments are described below:

Reaction between Tellurium tetrachloride and Phenylboric acid (1:1)

A mixture of tellurium tetrachloride (1.1 g, 4.0 mmol) and phenylboric acid (0.5 g, 4.0 mmol) in benzene (75 ml) was refluxed for two hours with constant stirring. The reaction mixture was cooled to room temperature and then filtered. The excess solvent was distilled from the filtrate under reduced pressure. The resulting white solid was recrystallized from absolute ethanol and was characterized as diphenyltellurium dichloride (0.03 g).

To a suspension of the residue (left after filtration) in diethylether (150 ml) was added a solution of potassium bisulfite (5.0 g) in water (150 ml) with constant stirring. Stirring was continued at room temperature overnight. The organic layer was separated and dried over anhydrous magnesium sulfate. After filtration, the excess diethylether was removed to give orange-red

Table II-C-5

Reactions of tellurium(IV) chloride and monoaryltellurium(IV) chlorides with arylelement(III) reagents

Reactants	Molar Ratio	Time (hrs.)	Compound Obtained	M.P. (°C) (lit. value)	Yield %
$TeCl_4$ + $PhB(OH)_2$	1:1	2	$PhTeCl_3$	---[a]	93
	1:2	20	Ph_2TeCl_2	158 (160)	78
	1:>2	20	Ph_2TeCl_2	158 (160)	78-80
$TeCl_4$ + Ph_2TlCl	1:1	---[b]	Ph_2TeCl_2	159 (160)	80
	1:1	5-6	Ph_2TeCl_2	158-59 (160)	80
$TeCl_4$ + $PhTlCl_2$	1:1	4	$PhTeCl_3$	---[a]	70
$C_2H_5OPhTeCl_3$ + $PhB(OH)_2$	1:1	20	$C_2H_5OPhTePh$ Cl_2	113 (113-15)	68
$C_2H_5OPhTeCl_3$ + Ph_2TlCl	1:1	6	$C_2H_5OPhTePh$ Cl_2	114 (113-15)	72

[a] Characterized as diphenylditelluride (see experimental).

[b] Carried out in solid-state (see experimental).

diphenylditelluride (0.75 g, 93 %; m.p., 63-65°C, Lit. (92) 66°C).

Reaction between Tellurium tetrachloride and Phenylboric acid (1:2)

Tellurium tetrachloride (1.1 g, 4.0 mmol) and phenylboric acid (1.0 g, 8.0 mmol) were refluxed in toluene (200 ml), for twenty hours with constant stirring. After cooling, the reaction mixture was filtered. The filtrate after removing excess solvent, gave the crude product. Washing this with cold methanol, (~ 2 ml), yielded pure diphenyltellurium dichloride.

Reaction between Tellurium tetrachloride and Diphenylthallium chloride (1:1)

(i) Tellurium tetrachloride (0.5 g, 2.0 mmol) and diphenylthallium chloride (0.8 g, 2.0 mmol) were carefully ground to a fine powder in a nitrogen filled glove bag. The mixture was transferred into a six inch long reaction tube having inlet and outlet valves to control the flow of nitrogen. The reactants were slowly heated to 140°C on an oil-bath. At ~ 130°C, the light yellow mixture turned into an intense yellow solid and a liquid of brown to red color. The contents were heated for a period of 30 minutes more at ~ 140°C and then allowed to cool to room temperature. The diphenyltellurium dichloride was extracted with chloroform and dried under vacuum.

The yellow solid, left after extraction, was characterized as thallous chloride.

(ii) A mixture of tellurium tetrachloride (1.1 g, 4.0 mmol) and diphenylthallium chloride (1.6 g, 4.0 mmol) in toluene (125 ml) was refluxed for 5-6 hours with constant stirring. The reaction mixture was allowed to cool to room temperature and then filtered. The filtrate on evaporation of excess solvent under reduced pressure gave diphenyltellurium dichloride. It was subsequently recrystallized from dry benzene or chloroform.

Reaction between (4-Ethoxyphenyl)tellurium trichloride and Diphenylthallium chloride (1:1)

A mixture of (4-ethoxyphenyl)tellurium trichloride (1.4 g, 4.0 mmol) and diphenylthallium chloride (1.6 g, 4.0 mmol) in toluene (100 ml) was refluxed for six hours with constant stirring. The reaction mixture was filtered cold. After distilling off excess solvent, the filtrate gave a viscous liquid which on standing in a freezer overnight crystallized. The phenyl(4-ethoxyphenyl)tellurium dichloride was recrystallized from benzene.

The white residue left after filtration was recrystallized from methanol and was characterized as phenylthallium dichloride.

REACTION WITH LEAD(II) DIETHYLDITHIOCARBAMATE

Various reactions, solvents, m.p.'s and yields are given in Table II C-6 and the typical experiments are described below:

Reaction between Tellurium tetrachloride and Lead bis(diethyldithiocarbamate) (1:2)

A mixture of tellurium tetrachloride (0.5 g, 2.0 mmol) and lead bis(diethyldithiocarbamate) (2.0 g, 4.0 mmol) in dry benzene (100 ml) was stirred for 4-6 hours and then filtered. After evaporating excess solvent, the filtrate gave bright yellow solid tellurium tetrakis(diethyldithiocarbamate). It was recrystallized from dry methylene dichloride and dried in vacuo at room temperature.

Reaction between Tellurium tetrachloride and Lead bis(diethyldithiocarbamate) (1:1)

To a solution of tellurium tetrachloride (0.5 g, 2.0 mmol) in benzene (75 ml) lead bis(diethyldithiocarbamate) (1.0 g, 2.0 mmol) was added in portions over a period of 15 min with constant stirring. The reaction mixture was stirred for a further two to three hours. It was worked up as described above to give the desired dichlorotellurium bis(diethyldithiocarbamate) in good yield.

Table II-C-6

Reactions of tellurium(IV) chloride and monoaryltellurium(IV) chlorides with lead(II) diethyldithiocarbamate

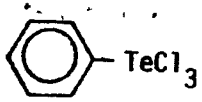
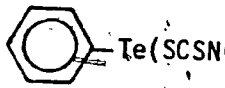
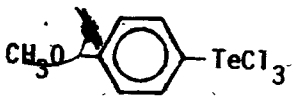
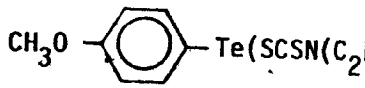
R_nTeCl_{4-n} used	Molar ratio	Tellurium compound obtained (color)	M.P. (°C) (lit. value)	Yield %
$TeCl_4$	1:1	$Cl_2Te(SCSN(C_2H_5)_2)_2$ [a] (yellow)	60-64	75
$TeCl_4$	1:2	$Te(SCSN(C_2H_5)_2)_4$ [b] (red)	103-104	81
	2:3	 [c] (yellow)	155 (156)	90
	2:3	 [d] (yellow)	166-168 (156-160)	95

Table II-C-6 (Contd.)

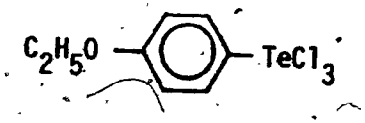
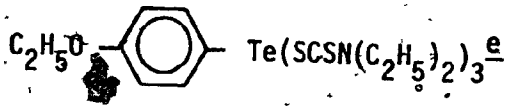
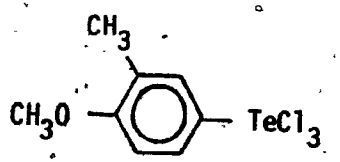
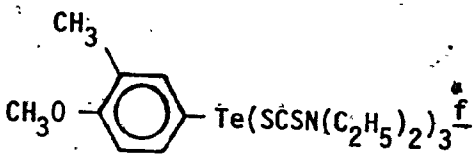
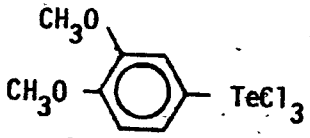
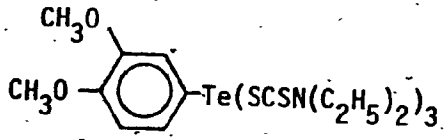
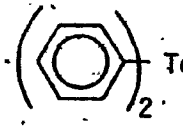
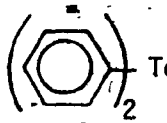
	2:3	 (yellow)	164-166	92
	2:3	 (yellow)	104-106	90
	2:3	 (dark red)	56-58	87

Table II-C-6 (Contd.)

	$TeCl_2$	1:1		98	50

[a] C = 32.09% (found), 33.33% (calcd.); H = 5.87% (found), 5.59% (calcd.).

[b] C = 24.57% (found), 24.25% (calcd.); H = 4.32% (found), 4.06% (calcd.).

[c] C = 38.59% (found), 38.83% (calcd.); H = 5.20% (found), 5.42% (calcd.).

[d] C = 40.04% (found), 39.82% (calcd.); H = 5.17% (found), 5.61% (calcd.).

[e] C = 39.39% (found), 39.83% (calcd.); H = 5.03% (found), 5.66% (calcd.).

[f] C = 39.71% (found), 39.83% (calcd.); H = 5.19% (found), 5.66% (calcd.).

[g] C = 44.53% (found), 45.70% (calcd.); H = 5.22% (found), 5.51% (calcd.).

Reaction between Phenyltellurium trichloride and Lead bis(diethyldithiocarbamate) (2:3)

A mixture of phenyltellurium trichloride (0.6 g, 2.0 mmol) and lead bis(diethyldithiocarbamate) (1.5 g, 3.0 mmol) in dry benzene (150) was stirred for four hours. Filtration followed by evaporation of excess solvent gave a yellow viscous liquid which on treatment with absolute methanol turned into a yellow solid. It was recrystallized from dry CH_2Cl_2 and was characterized as phenyltellurium tris(diethyldithiocarbamate).

REACTION WITH LEAD(II) BENZENETHIOLATE

Various reactions of tellurium tetrachloride and monoaryltellurium trichlorides are summarized in Table II-C-7. The experimental details for some typical reactions are described here.

Reaction between Tellurium tetrachloride and Lead bis(benzenethiolate) (1:2)

(i) at ~ 25°C: To a solution of tellurium tetrachloride (0.5 g, 2.0 mmol) in carbon tetrachloride or benzene (70 ml) lead bis(benzenethiolate) (1.7 g, 4.0 mmol) was added in portions with constant stirring. Mixed black and white solids immediately precipitated. The reaction mixture was stirred for one additional hour and then filtered. The

filtrate, on evaporating excess solvent, gave a yellow solid which was found by thin-layer chromatography to contain biphenyldisulfide and a small amount of the desired product. The solid was exposed to the atmosphere and was then treated with water. The yellow crude biphenyldisulfide was extracted with diethylether and was recrystallized from absolute ethanol. The black material was identified as elemental tellurium.

The residue left after extraction was characterized as lead dichloride and elemental tellurium.

(ii) <u>at ∿ - 63 °C</u>: Lead bis(benzenethiolate) (1.7 g, 4.0 mmol) and tellurium tetrachloride (0.75 g, 2.0 mmol) in dry ether or methylene dichloride (100 ml) were mixed in the same manner as described above at ∿ - 63 °C. After about two hours of stirring, the yellow color of lead bis(benzenethiolate) had disappeared and the solution turned intense yellow. The mixture was filtered through a medium frit funnel under nitrogen into a two-necked, round-bottom flask kept at ∿ - 63 °C. The excess solvent was evaporated under high vacuum, while keeping the temperature below 0 °C. The tellurium tetrakis(benzenethiolate) was obtained in almost quantitative yield.

<u>Reaction between (4-Ethoxyphenyl-)tellurium trichloride and Lead bis(benzenethiolate) (2:3)</u>

To a suspension of lead bis(benzenethiolate)

Table II-C-7

Reactions of tellurium(IV) chloride and monoaryltellurium(IV) chlorides with lead(II) benzenethiolate or triphenyllead benzenethiolate

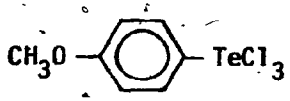
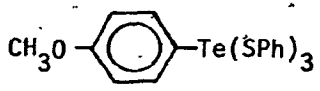
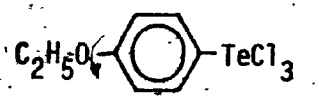
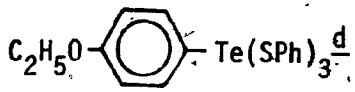
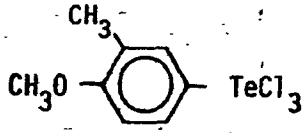
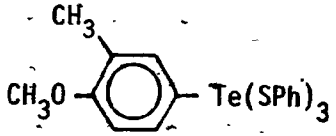
Tellurium compound (molar ratio)	Temp. (°C)/ solvent	Product obtained	Organotellurium or organic compd. M.P. (°C)	Yield %
With $Pb(SPh)_2$				
$TeCl_4$ (1:1)	r.t.[a]/Bz or CCl_4	PhS-SPh	61 (60-63)	95
(1:1)[b]	∿-63/Ether	PhS-SPh		
(1:2)	r.t./Bz or CCl_4	PhS-SPh		
(1:2)	∿-22/$CHCl_3$	PhS-SPh		
(1:2)	∿-63/Ether	$Te(SPh)_4$	100(dec.) (102)(dec.)	100
 (2:3)	∿-63/Ether		c	85

Table II-C-7 (Contd.)

 (2:3)	~-63/Ether		48-50	90
 (2:3)	r.t./CCl_4 or $CHCl_3$		40	95
With Ph_3Pb/SPh				
Ph_2TeCl_2 (1:2)	r.t./CCl_4	Ph_3PbCl	208	95
		Ph_2Te	150	92
		PhS-SPh	61	90

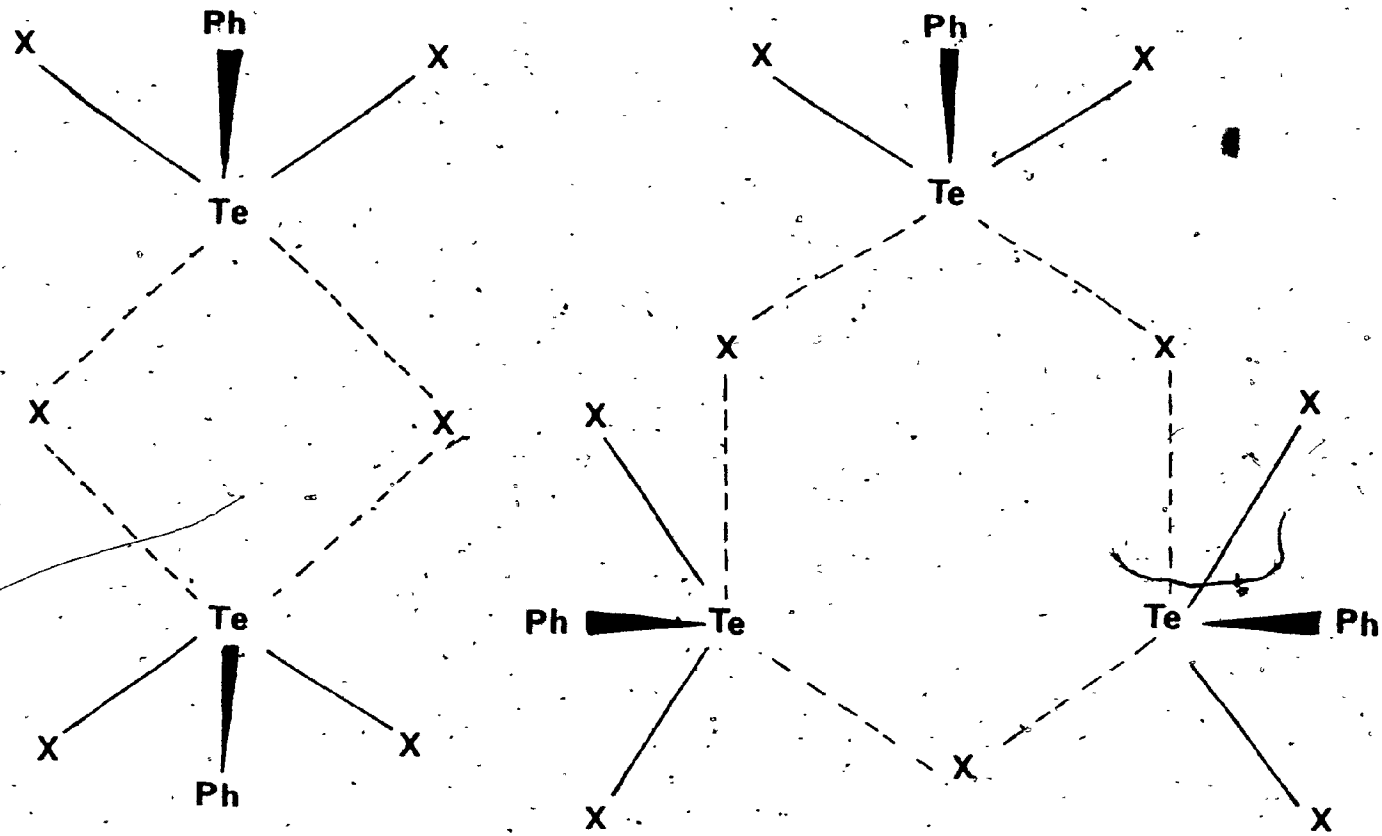


Figure III-2: Typical structures resulting from donor-acceptor interaction of $RTeX_2^+$ and X^- (173)

The first example of an X-ray crystal structure of a trihalide was recorded in 1971 by Kobelt and Paulus (175). They reported that the crystals of (2-chloroethyl)tellurium trichloride consist of a polymeric chain held by bridging chlorine atoms with the five coordinated tellurium atom situated nearly in the centre of the base of a square-pyramid. On the basis of crystal data, a somewhat ionic lattice with $ClCH_2CH_2TeCl_2^+$ and Cl^- ions alternating along the polymer chain has been suggested for the compound. The structure of (2-chloroethyl)tellurium trichloride is depicted in Figure III-3.

Hazell (176) has determined the structure of an addition product of the reaction between tellurium tetrabromide and cyclohexene. He found that the compound, formulated by Aynsely (177) as $(TeBrC_6H_{10})_x$, displays essentially symmetrical bromine bridging.

Recently, McCullough and coworkers (178-180) investigated the structures of (2-biphenylyl)tellurium tribromide (178) and of the α- and β-modifications of the triiodide analog (179,180). Unlike (2-chloroethyl)tellurium trichloride (175), these compounds have been found to be discrete monomers with an unexpected, weak interaction between the tellurium and a formally non-bonded aryl carbon atom. The geometry about the tellurium atom in the three compounds is reported to be essentially trigonal-bipyramidal. The molecular structures and the unit cell packing diagrams of the tribromide and the triiodides are reproduced in Figures III-4 to III-6, respectively.

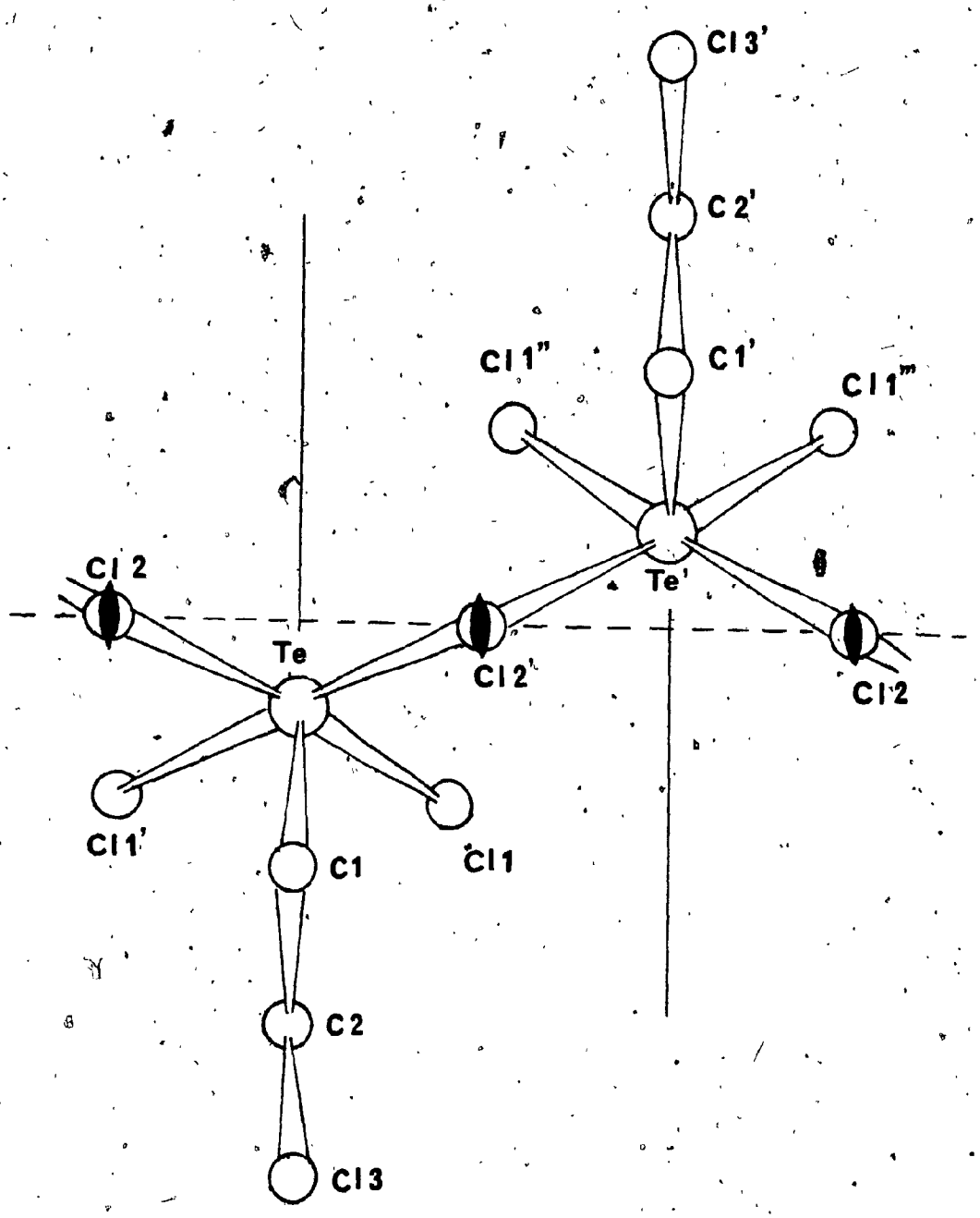
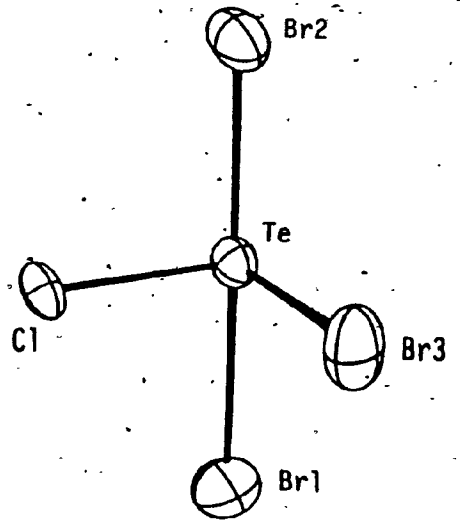
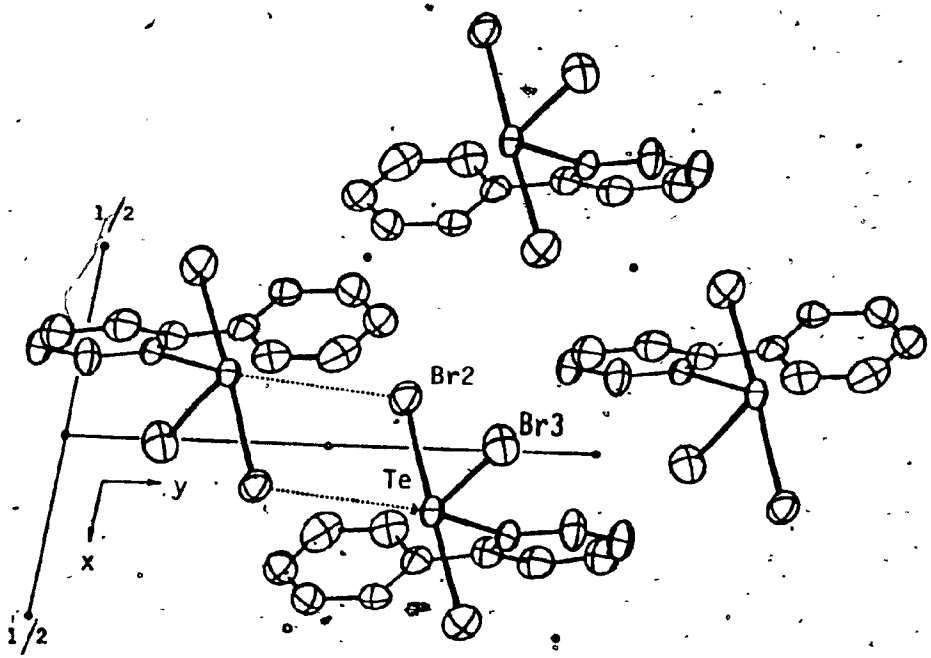


Figure III-3: Crystal structure of $(2\text{-}ClCH_2CH_2)TeCl_3$ (175)



(A)



(B)

Figure III-4: The molecular structure (A) and unit cell packing diagram (B) of (2-biphenylyl)tellurium tribromide (178).

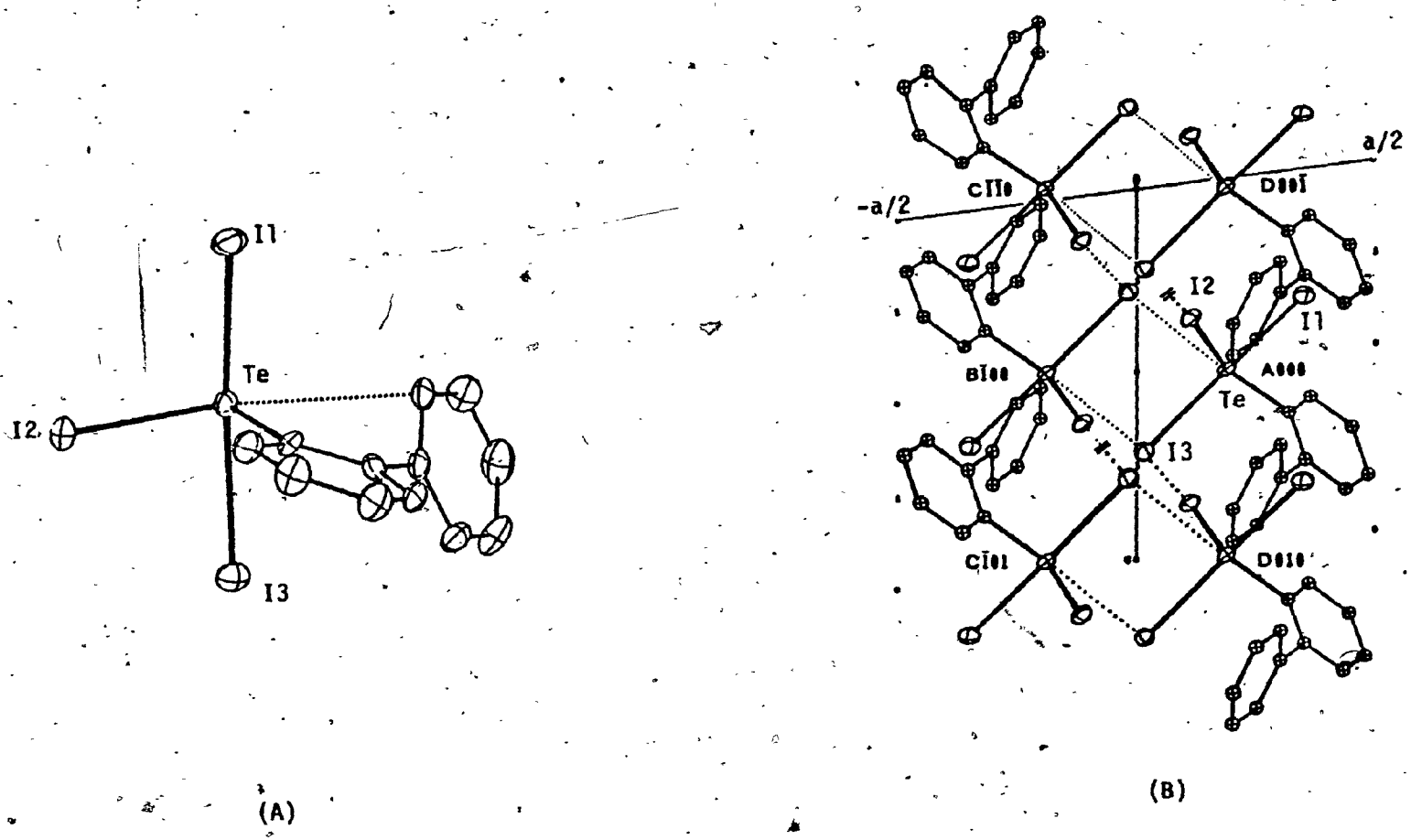
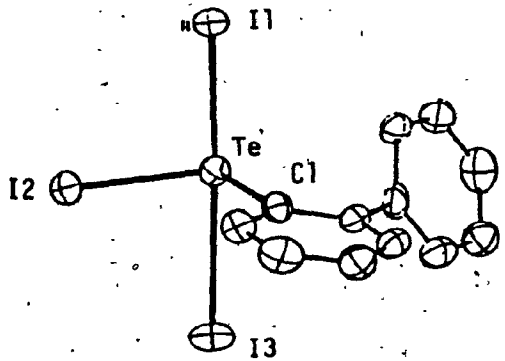
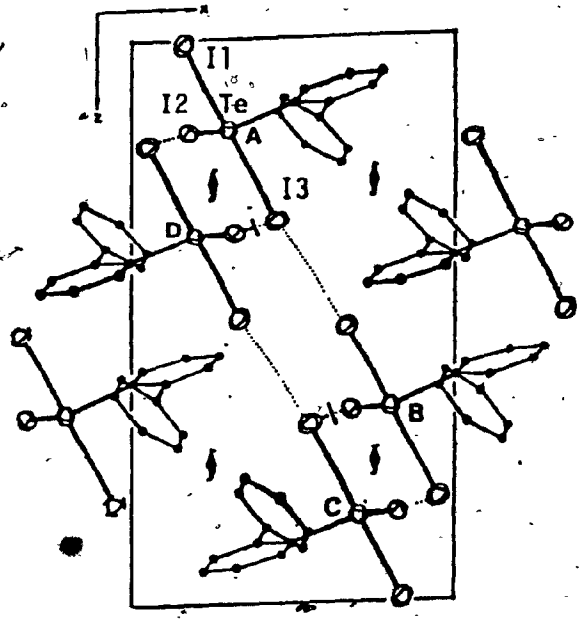


Figure III-5: The molecular structure (A) and unit cell packing diagram (B) of β-(2-biphenylyl)tellurium triiodide (180).



(A)



(B)

Figure III-6: The molecular structure (A) and unit cell packing diagram (B) of α - (2-biphenylyl)tellurium triiodide (179).

More recently, in this laboratory, an X-ray structure of (4-methoxyphenyl)tellurium triiodide was determined (181) and a dimeric structure similar to that predicted by vibrational spectroscopy (173) and molecular weight determination (172) was observed. As a continuation of this study, the structures of (4-ethoxyphenyl)tellurium trichloride and -tribromide were investigated by the author and the results presented in this chapter of the thesis. Since the tribromide exhibited a similar structure to that of the triiodide determined by Bird (181), the crystal data and the results of the latter are also included in the discussion with the tribromide.

An up-to-date list of reported values for Te-C and Te-X (X = Cl, Br, or I) bond lengths and non-bonded intermolecular contacts in organotellurium halides is given in Table III-1.

Table III-1

Literature values for some bond lengths and important intermolecular contacts (Å) in organotellurium halides

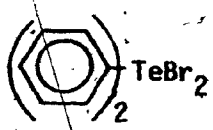
Compound	Te-C (alkyl or aryl)	X=Cl, Br or I			References
		Te-X	Te'-X	X-X	
Chlorides					
$(CH_3)_2TeCl_2$	2.08 2.10	2.48 2.54	3.46	-	162
$(ClCH_2CH_2)_2TeCl_2$	2.15 2.15	2.48 2.52	-	-	169
$(ClCH_2CH_2)TeCl_3$	2.16	2.39 2.72	-	-	175
$(ClC_6H_{10})_2TeCl_2$	2.18	2.47 2.52	-	-	170
$ClC_6H_{10}(4\text{-}CH_3C_6H_4)TeCl_2$	2.24	2.47 2.50	-	-	171
Bromides					
	2.18	2.68	-	-	161

Table III-1 (Contd.)

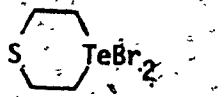
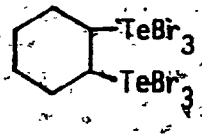
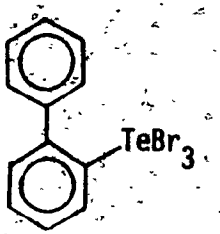
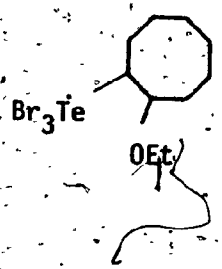
	2.14 2.16	2.66 2.69	- 3.59	-	168
	2.19 2.25	2.54 2.88	-	-	176
	2.14	2.49 2.65 2.68	3.71	-	178
	2.29	2.65 2.67 2.50	-	-	182

Table III-1 (Contd.)

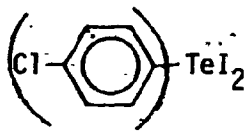
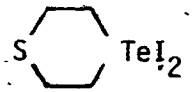
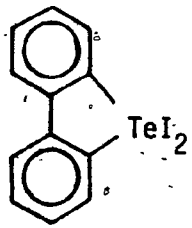
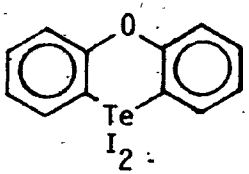
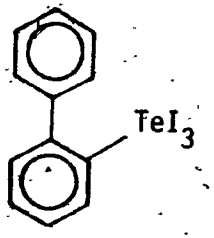
Iodides					
α-$(CH_3)_2TeI_2$	2.12 2.13	2.97 2.89	3.90	-	158
	2.12 2.10	2.91 2.93	3.92 3.91	-	
	2.13 2.16	2.85 2.99	3.66 4.03	-	
β-$(CH_3)_2TeI_2$	2.01	2.84	-	-	158
$[(CH_3)_3Te]^+[CH_3TeI_4]^-$	2.08	2.89			
	2.13 2.15	2.95 2.98	-		
	2.10 2.13	2.92 2.95	4.46 4.13	4.32 4.10	160
	2.15 2.17	2.88 2.93	3.81 3.69	-	43
	2.13 2.18	2.88 2.94	3.76 4.13 4.16	-	165
	2.15 2.16	2.98 2.85	4.30 3.95	-	

Table III-1 (Contd.)

		2.11 2.11	2.94 2.93	3.72 3.69	-	166
		2.11 2.09	2.94 2.95	3.74 3.79	-	167
$(CH_3)_2TeI_4$		2.14 2.15	3.08 2.81	- 3.57	3.40 3.46	183
	(α-form)	2.15	2.83 2.77 2.10	- -	3.77 3.24	179
	(β-form)	2.15	2.83 2.75 3.03	3.70	3.34	180

RESULTS AND DISCUSSION

The Crystal and Molecular Structure of (4-ethoxyphenyl)tellurium trichloride, $(4\text{-}C_2H_5OPh)TeCl_3$.

The compound crystallizes as the non-centrosymmetric monochloro-bridged polymer shown in Figure III-7, which depicts a stereographic view of the cell as viewed down the c axis: the bridging between the neighbouring molecules is such that the chain propagates along this axis. A perspective view of the two formula units linked through one chlorine atom showing the labelling system is depicted in Figure III-8. Selected distances and angles are listed in Table III-2.

Each tellurium atom has square-pyramidal coordination, with the 4-ethoxyphenyl group in the apical position, and the chlorines at the basal corners. The pyramids are joined through the cis basal chlorine atoms. The polymeric structure is essentially identical with that of (2-chloroethyl)tellurium trichloride (175). In (4-ethoxyphenyl)tellurium trichloride, the terminal and bridging Te-Cl bond lengths average 2.396(6) and 2.749(5) Å, respectively, while the analogous distances in $2\text{-}ClCH_2CH_2TeCl_3$ are 2.386 and 2.717 Å, both slightly shorter. The difference is rationalized in terms of the more electron releasing character of 4-ethoxyphenyl group. Unfortunately the structure determinations are

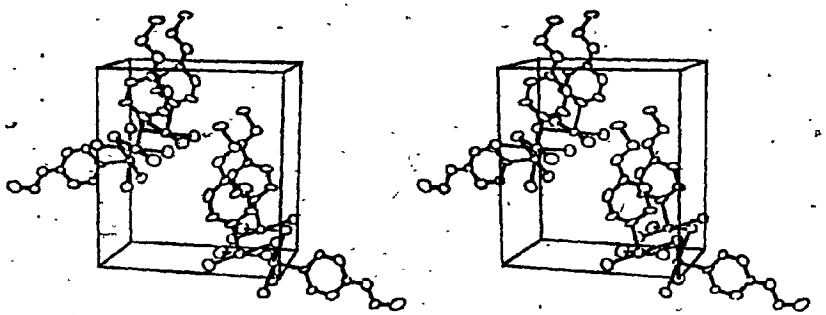


Figure III-7: Unit cell packing of (4-EtOPh)$TeCl_3$ as viewed down the c axis.

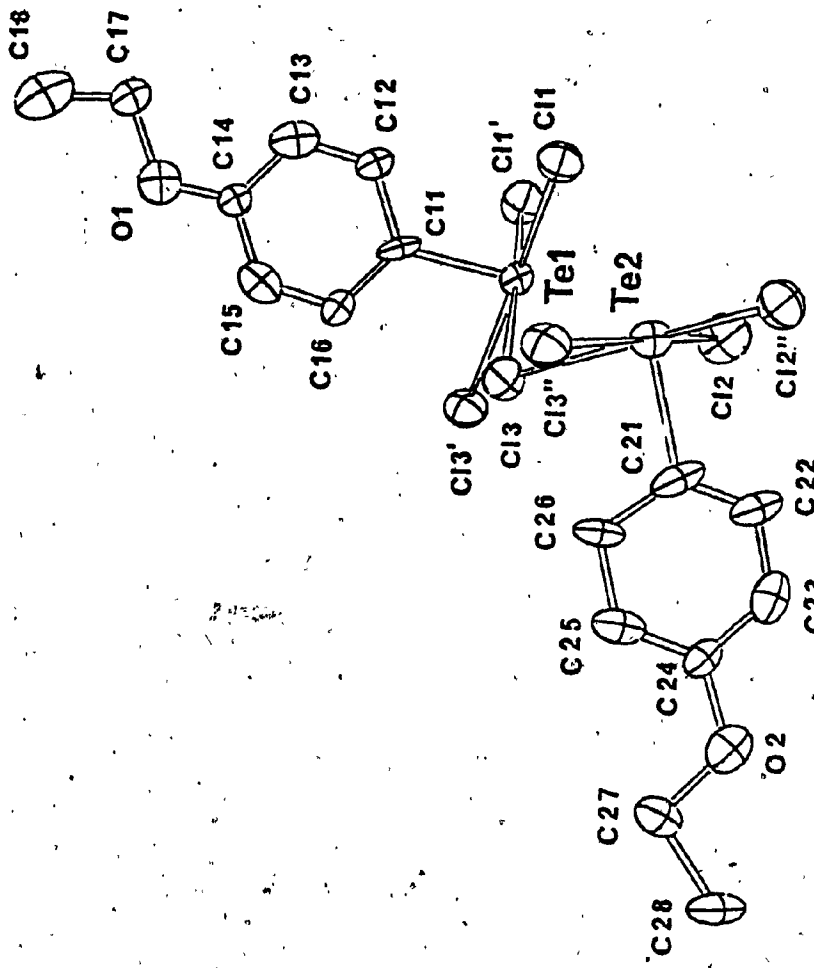


Figure III-8: (4-EtOPh)$TeCl_3$ atom labelling scheme.

Table III-2

Bond lengths (Å) and angles (deg) in (4-EtOPh)$TeCl_3$

Distances

Te1-Cℓ1	2.397(6)	Te2-Cℓ2	2.395(6)
Te1-Cℓ3	2.740(5)	Te2-Cℓ3	2.757(5)
Te1-C11	2.09(3)	Te2-C21	2.16(3)
C11-C12	1.44(5)	C21-C22	1.31(7)
C12-C13	1.38(5)	C22-C23	1.36(6)
C13-C14	1.42(6)	C23-C24	1.42(6)
C14-C15	1.39(5)	C24-C25	1.38(5)
C15-C16	1.35(6)	C25-C26	1.43(6)
C16-C11	1.42(5)	C26-C21	1.49(7)
C14-01	1.29(5)	C24-02	1.39(6)
01-C17	1.46(6)	02-C27	1.48(7)
C17-C18	1.44(6)	C27-C28	1.59(7)

Angles

Te1-Cℓ3-Te2 = 101.8(2)

Cℓ1-Te1-Cℓ3	90.3(2)	Cℓ2-Te2-Cℓ3	92.1(2)
Cℓ1-Te1-Cℓ1'	92.4(2)	Cℓ2-Te2-Cℓ2"	92.8(2)
Cℓ1-Te1-Cℓ3'	177.0(2)	Cℓ2-Te2-Cℓ3"	175.1(2)
Cℓ3-Te1-Cℓ3'	87.0(2)	Cℓ3-Te2-Cℓ3"	83.0(2)
Cℓ1-Te1-C11	91.8(5)	Cℓ2-Te2-C21	90.2(7)
Cℓ3-Te1-C11	86.8(5)	Cℓ3-Te2-C21	89.6(7)
C16-C11-C12	118(1)	C26-C21-C22	128(2)
C11-C12-C13	121(2)	C21-C22-C23	117(2)
C12-C13-C14	119(1)	C22-C23-C24	122(2)

Table III-2 (Contd.)

C13-C14-C15	118(2)	C23-C24-C25	120(2)
C14-C15-C16	124(2)	C24-C25-C26	122(2)
C15-C16-C11	118(2)	C25-C26-C21	111(2)
Te1-C11-C12	119(1)	Te2-C21-C22	119(1)
Te1-C11-C16	123(1)	Te2-C21-C26	113(1)
C13-C14-O1	122(1)	C23-C24-O2	114(1)
C15-C14-O1	119(2)	C25-C24-O2	125(2)
C14-O1-C17	121(2)	C24-O2-C27	116(2)
O1-C17-C18	109(2)	O2-C27-C28	99(2)

not sufficiently accurate to permit the observation of the differences in the Te-C bond orders which might have supported this hypothesis. In tellurium tetrachloride (184) which is tetrameric in the crystalline state and possesses a cubane type structure, the average Te-Cl(bridging) distance is 2.93 Å; 0.6 Å longer than the Te-Cl(terminal) bond lengths.

In both structures, the tellurium atoms are found lying almost exactly in the basal planes formed by the chlorine atoms: 0.004 and 0.029 Å below the plane, (relative to the apical carbon atom) in (4-EtOPh)$TeCl_3$ and 0.10 Å below this plane in (2-$ClCH_2CH_2$)$TeCl_3$. The Te-C bond distances in the two compounds average 2.10 and 2.16 Å, respectively. Angular distortion is such that the C-Te-Cl(bridging) angles are smaller than C-Te-Cl(terminal) angles in both compounds: in (4-EtOPh)$TeCl_3$ these angles average 88.2(6) and 91.0(6)°, respectively, while in (2-$ClCH_2CH_2$)$TeCl_3$ the difference is slightly larger; 82.5 vs. 92.7°. This reduction in angles can be attributed to relatively stronger bond-pair repulsion between Te-C and Te-Cl(terminal) bonds than the Te-C and Te-Cl(bridging).

Perhaps the most striking feature in both the trichloride structures is the very acute angle between the basal planes of the pyramids. In (4-ethoxyphenyl)tellurium trichloride this angle is 63.3°. This presumably results from weak bonding, the short distances between adjacent tellurium atoms, 4.265(2) Å, and between

one tellurium atom and terminal chlorines of the neighbouring tellurium atoms, 3.854(3) and 3.833(3) Å are a symptom of this (The van der Waals contacts would be 4.4 and 4.0 Å, respectively). A dibridged dimeric structure similar to that displayed by the tribromide, which is described in section B of this chapter, has been suggested for CH_3TeCl_3 on the basis of molecular weight determination in solution. Such a structure would probably be precluded by excessively short Te--Te or Cl--Cl distances across the four-membered bridged system.

The polymeric chains of the structure are packed together such that the remaining contacts, at normal van der Waals distances, occur between the 4-ethoxyphenyl moieties which are interleaved with others of neighbouring chains and between 4-ethoxyphenyl groups and the terminal chlorine atoms also on neighbouring chains. The C-C bond distances and C-C-C angles which range from 1.31(7) to 1.49(7) Å and 111(2) to 128(2)°, respectively, are normal for this kind of structure.

The Crystal and Molecular Structure of (4-ethoxyphenyl)tellurium tribromide, $(4\text{-}C_2H_5OPh)TeBr_3$.

Although the tribromide which was investigated in the present study is not isomorphous with (4-methoxyphenyl)tellurium triiodide (181), it has sufficient similar features to be considered approximately isostructural. In both cases, the two halogen atoms of a monomer interact with the adjacent tellurium to form a discrete dibridged dimeric molecule. The coordination at each tellurium is square-pyramidal, with the halogen atoms in the basal plane and the organic group apical. The aryl groups are cisoid and the dihedral angle between the pair of pyramid bases are 1.2 and 5.2° for the bromide and iodide compounds, respectively.

The structures of the dimeric units along with the atom labelling scheme are shown in Figures III-9 and III-10. The packing diagrams, Figures III-11 and III-12, illustrate the base-to-base association of dimers. This association of the bromide and iodide differs: this is shown in Figures III-13 and III-14 which depict projections perpendicular to the basal planes. A projection along the Te-Te vector in $(4\text{-EtOPh})TeBr_3$ is illustrated in Figure III-15. The corresponding bond distances and angles for the two compounds are collected in Table III-3.

The dimeric units observed for the bromide and for the iodide(181) represent a structural type which seems

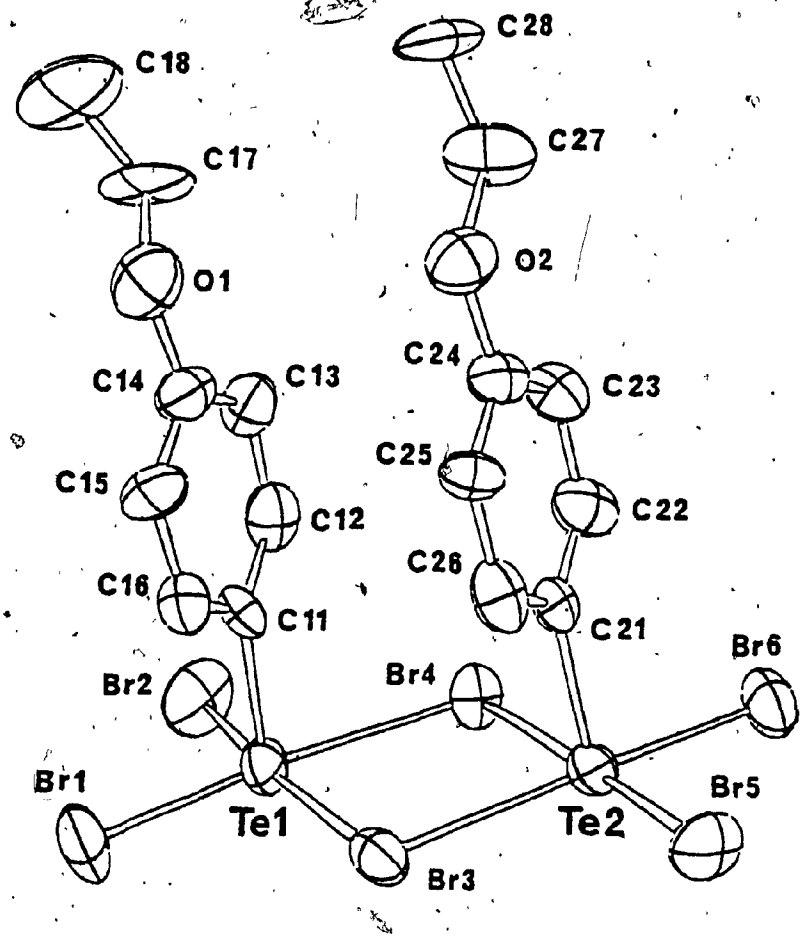


Figure III-9: (4-EtOPh)$TeBr_3$ dimer with atom labelling scheme.

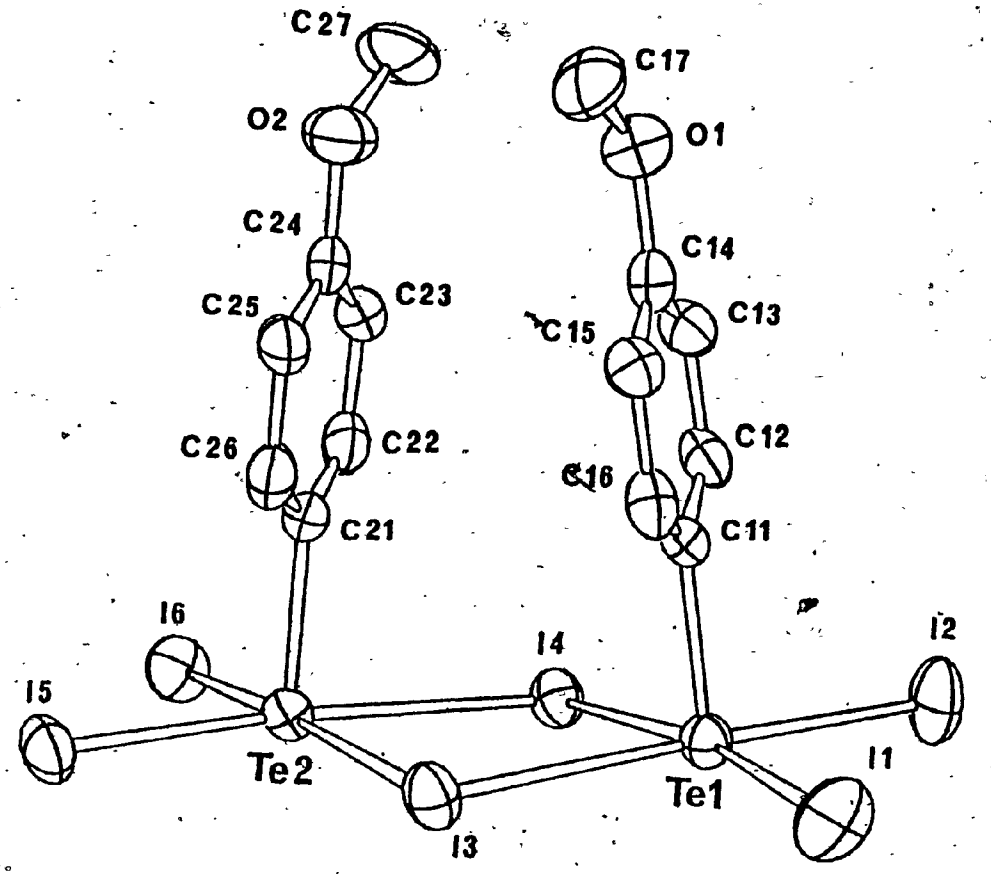


Figure III-10: (4-MeOPh)TeI_3 dimer with atom labelling scheme.

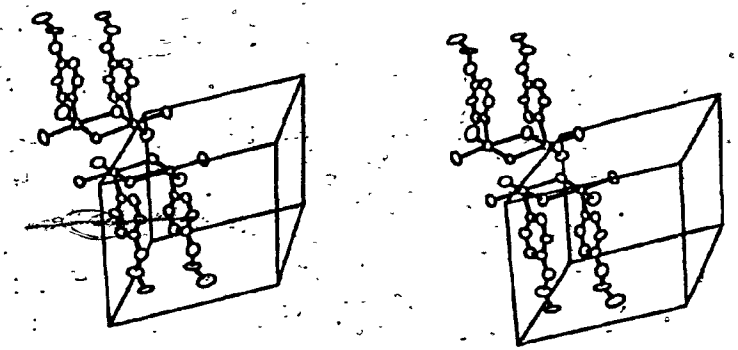


Figure III-11: Unit cell packing of (4-EtOPh)$TeBr_3$.

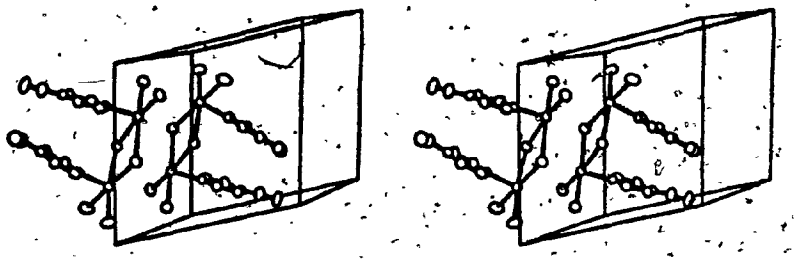


Figure III-12: Unit cell packing of (4-MeOPh)TeI_3

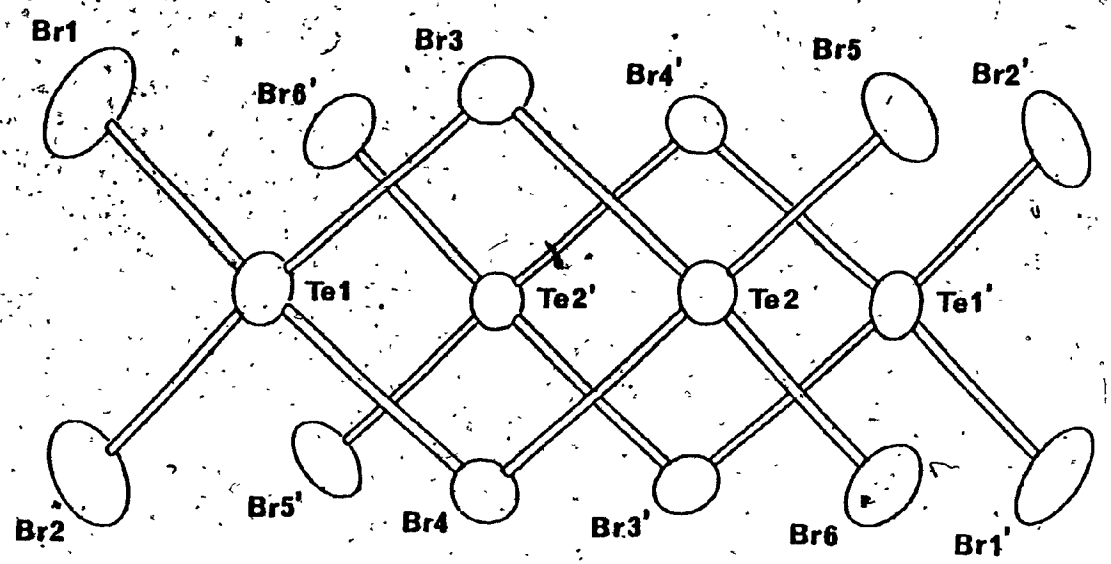


Figure III-13: Juxtaposition of the basal planes of the dimers in (4-EtOPh)$TeBr_3$.

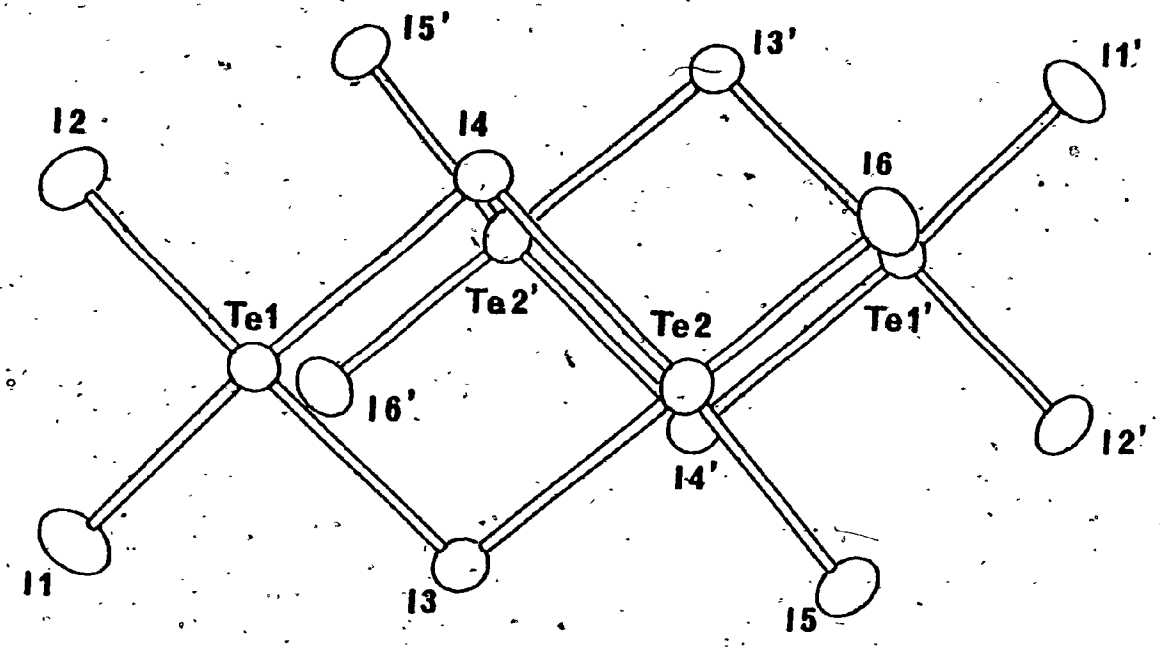


Figure III-14: Juxtaposition of the basal planes of the dimers in (4-MeOPh)TeI_3

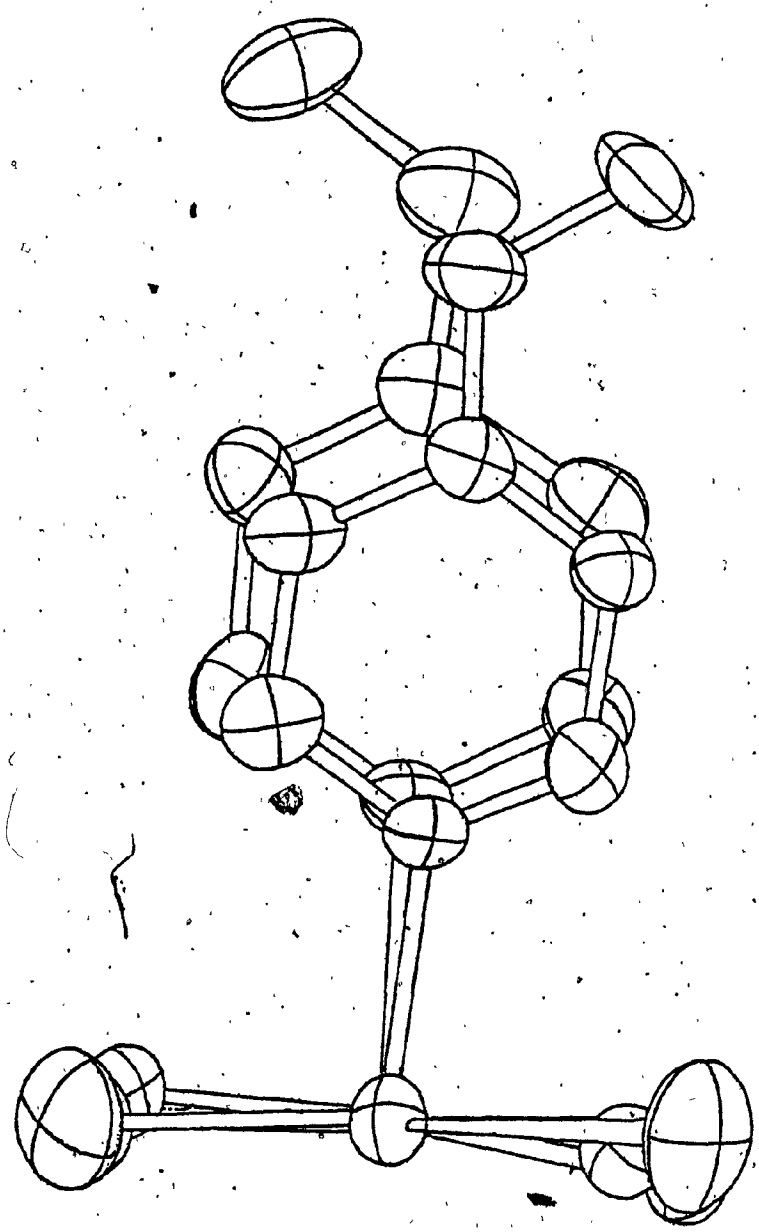


Figure III-15: A projection along the Te-Te vector in (4-EtOPh)$TeBr_3$.

Table III-3

Bond lengths (Å) and angles (deg) in (4-EtOPh)$TeBr_3$ and (4-MeOPh)TeI_3

Distances

	(4-EtOPh)$TeBr_3$	(4-MeOPh)TeI_3		(4-EtOPh)$TeBr_3$	(4-MeOPh)TeI_3
Te1-X1	2.527(3)	2.776(1)	Te2-X3	2.884(2)	3.146(9)
Te1-X2	2.509(3)	2.797(1)	Te2-X4	2.912(2)	3.177(1)
Te1-X3	2.992(3)	3.097(1)	Te2-X5	2.539(2)	2.783(1)
Te1-X4	2.940(3)	3.192(1)	Te2-X6	2.548(2)	2.797(1)
Te1-C11	2.09(2)	2.14(1)	Te2-C21	2.11(1)	2.16(1)
C11-C12	1.38(2)	1.37(2)	C21-C22	1.41(2)	1.32(2)
C12-C13	1.43(3)	1.42(2)	C22-C23	1.41(3)	1.45(2)
C13-C14	1.42(3)	1.39(2)	C23-C24	1.39(2)	1.35(2)
C14-C15	1.39(3)	1.38(2)	C24-C25	1.37(2)	1.43(2)
C15-C16	1.38(3)	1.41(2)	C25-C26	1.42(2)	1.39(3)
C16-C11	1.39(2)	1.37(2)	C26-C21	1.38(2)	1.41(2)
C14-O1	1.38(2)	1.35(1)	C24-O2	1.39(2)	1.36(1)
O1-C17	1.49(2)	1.45(2)	O2-C27	1.48(2)	1.44(2)
C17-C18	1.41(4)		C27-C28	1.50(3)	

Table III-3 (Contd.)

Te1-X3-Te2	93.56(7)	94.47(3)	Te1-X4-Te2	94.09(7)	92.05(3)
X1-Te1-X2	95.16(10)	92.87(4)	X3-Te2-X4	87.35(7)	85.94(3)
X1-Te1-X3	90.57(9)	88.94(4)	X3-Te2-X5	91.60(8)	88.30(3)
X1-Te1-X4	174.70(9)	171.47(4)	X3-Te2-X6	175.22(8)	174.62(4)
X2-Te1-X3	173.90(9)	177.05(4)	X4-Te2-X5	178.61(8)	173.59(4)
X2-Te1-X4	89.29(8)	91.39(3)	X4-Te2-X6	88.98(7)	92.45(3)
X3-Te1-X4	84.88(6)	86.52(3)	X5-Te2-X6	92.02(8)	93.04(3)
X1-Te1-C11	92.7(4)	95.9(3)	X3-Te2-C21	88.4(4)	91.1(3)
X2-Te1-C11	94.1(4)	93.5(3)	X4-Te2-C21	87.7(4)	87.9(3)
X3-Te1-C11	87.7(4)	88.6(3)	X5-Te2-C21	93.1(4)	95.0(3)
X4-Te1-C11	89.8(4)	91.2(3)	X6-Te2-C21	94.5(4)	94.0(3)
C16-C11-C12	121(3)	123(1)	C26-C21-C22	122(2)	124(1)
C11-C12-C13	121(2)	117(1)	C21-C22-C23	119(2)	119(1)
C12-C13-C14	116(2)	120(1)	C22-C23-C24	118(2)	118(1)
C13-C14-C15	123(2)	120(1)	C23-C24-C25	123(2)	122(1)
C14-C15-C16	118(2)	120(1)	C24-C25-C26	119(2)	119(1)
C15-C16-C11	121(2)	118(1)	C25-C26-C21	121(2)	117(1)

Table III-3 (Contd.)

Te1-C11-C16	120(1)	119(1)	Te2-C21-C26	120(1)	117(1)
Te1-C11-C12	118(1)	117(1)	Te2-C21-C22	118(1)	119(1)
C13-C14-01	121(2)	115(1)	C23-C24-02	121(1)	125(1)
C15-C14-01	116(2)	125(1)	C25-C24-02	115(1)	113(1)
C14-01-C17	118(1)	118(1)	C24-02-C27	119(1)	118(1)
01-C17-C18	105(2)	-	02-C27-C28	104(2)	-

uncommon, although vibrational spectroscopy has predicted this type of association in other aryltellurium trihalides (170). The only other structure described in the literature, which is similar to the tribromide, is the 1,2-cyclohexylenebridged, $Te_2Br_6C_6H_{10}$, obtained from cyclohexene and $TeBr_4$ (176). A survey (Table III-1) of the non-ionic dibromides, R_2TeBr_2, (161,168) and tribromides (176,178) shows these compounds to be essentially monomeric with weak but significant intermolecular interaction as short as 3.591 Å (c.f. the van der Waals contact of 4.15 Å). The diiodides (43,158-160, 165-167,183) and triiodides (178,179) show similar, but perhaps stronger Te--I interactions (between otherwise monomeric species) as short as 3.692 Å, and I--I distances as low as 3.239 Å (179) (c.f. van der Waals contacts of 4.35 and 4.30 Å, respectively). By comparison, the analogous contacts between dimeric units in (4-EtOPh)$TeBr_3$ are very long, i.e., Te1--Br5', 4.117(2); Te1--Br6', 4.054(2); Te2--Br3', 4.226; and Te2--Br4', 4.119 Å (representing only the slightest of interactions). Nevertheless, the Te1--Te2' distance of 4.173(2) Å is significantly less than the normal Te--Te van der Waals contact of 4.40 Å. In (4-MeOPh)TeI_3 the interdimer interactions appear stronger: the Te1--I6' and Te2--I4' distances are 3.874 and 3.779 Å, respectively, although Te1 and Te2 of the other dimer unit are not in contact. The interaction between the dimeric units is further manifest in the larger fold (see above) between the pyramid bases found in the triiodide. This results from the weak bonding of the bridging iodines to a third tellurium atom. The molecule

$Te_2Br_6C_6H_{10}$ (176), which also possesses bridging halogen atoms, reveals certain differences which might be ascribed to the constraint of the cyclohexylene group; thus, the dihedral angle between the pyramid bases is ca. 53°, the Te-Br(bridge) distances are shorter (2.870 and 2.890(8) Å) than those in (4-EtOPh)$TeBr_3$ (2.884 to 2.992(2) Å), and interestingly, there are very short Br--Br intermolecular interactions of a type absent in (4-EtOPh)$TeBr_3$ Br(terminal)--Br(terminal) minimum 3.55 Å; Br(terminal)--Br(bridge) minimum 3.59 Å (a normal Br--Br van der Waals contact is 3.90 Å).

Terminal halogen-to-tellurium distances vary over a very large range: from 2.490 A to 2.675 Å for Te-Br and from 2.769 to 3.099 Å for Te-I. Evidently such bonds are easily deformed by inter- and intra-molcular influences, but the literature contains too few examples for a detailed analysis. The bond distances observed in (4-EtOPh)$TeBr_3$, which range from 2.509 to 2.548(2) Å, and those found in (4-MeOPh)TeI_3, ranging from 2.776(1) to 2.797(1) Å, are all within the previously observed limits.

The Te-C bond length in the tribromide and triiodide lie between 2.01(2) to 2.16(1) Å.

EXPERIMENTAL

GENERAL TECHNIQUES

Instruments

Weissenberg and Precession Cameras were made by the Charles Supper Co., Natick, Mass., U.S.A. and were used to collect photographic data, in conjuction with a fine focus molybdenum target X-ray tube, powered by a Picker Nuclear generator and control model No. 809B operated at 40 kV and 20 mA. "No Screen" X-ray film was used.

A four-circle Picker Nuclear FACS-1 Diffractometer, operated by a P.D.P. 8/S dedicated minicomputer, was used to collect the intensity data. The Mo target X-ray tube was powered at 20 mA and 40 kV using a Picker Nuclear constant potential generator model 6238E (stable to within 0.1 % kV and 0.2 % mA). The take off angle was 3° and the K_{α} line was selected using the (002) planes of a Graphite "crystal". The distance between monochromator and the sample crystal was 14.0 cm. The receiving aperture, the size of which was determined by horizontal and vertical slits, was located at 23.0 cm from the crystal and 20 mm from a scintillation counter.

A series of three nickel foils on a rotating disc were used as the attenuators. The detector was operated at about 1000 volts and the pulse height analyzer was set to receive 100 % of the X-ray intensity. Thus, a scan using a 0.2 KeV window (upper level setting of 2.0 and 10 % mode), of peak intensity versus baseline discriminator level was recorded from 10.0 KeV to 0.6 KeV. The differential pulse height distribution curve so obtained was used to establish the upper and lower level of discriminator voltage.

Photographic Data Collection

A single crystal of suitable size, chosen under a microscope, was mounted on a borosilicate glass fibre, which was in turn fixed using epoxy glue to a copper wire extending out from the Goniometer head. After the glue had dried the Goniometer head was fixed onto the rotating spindle of the Weissenberg camera and the crystal was centered visually.

In order to align the crystal such that a direct crystal axis is parallel to the axis of rotation, rotation pictures with 10° oscillation at an azimuthal value of 180 and 270° were taken. The correction needed was made on the Goniometer arcs and a final alignment picture with the screen was taken. Once the crystal was perfectly aligned, the Weissenberg zero and first layer photographs were taken.

Subsequently, the Goniometer was transferred to the Precession camera. After aligning the crystal on one of the axes chosen from the zero-level Weissenberg picture, the two photographs corresponding to zero- and first-levels were taken at a precession angle of 20° . These two zones were also photographed for the other axis. The relationship between the film measured spacing, Y_n, and the reciprocal cell constants for the precession camera can be written, thus:

$$d^* = \frac{Y_n}{60.0\,\lambda} \qquad \text{(III-1)}$$

where λ (= 0.71069 Å) is the wavelength of the molybdenum K_α/K_β radiation filtered with zirconium foil. A schematic representation of this relationship is shown in Figure III-16.

The symmetry and the systematic absences appearing on the Weissenberg and precession photographs were used to deduce the space group of the crystal, while the length of the three reciprocal cell edges and the angles between them were used to compute the direct unit cell parameters. All measurements of distances and angles were carried out using a Charles Supper Co. film measuring device.

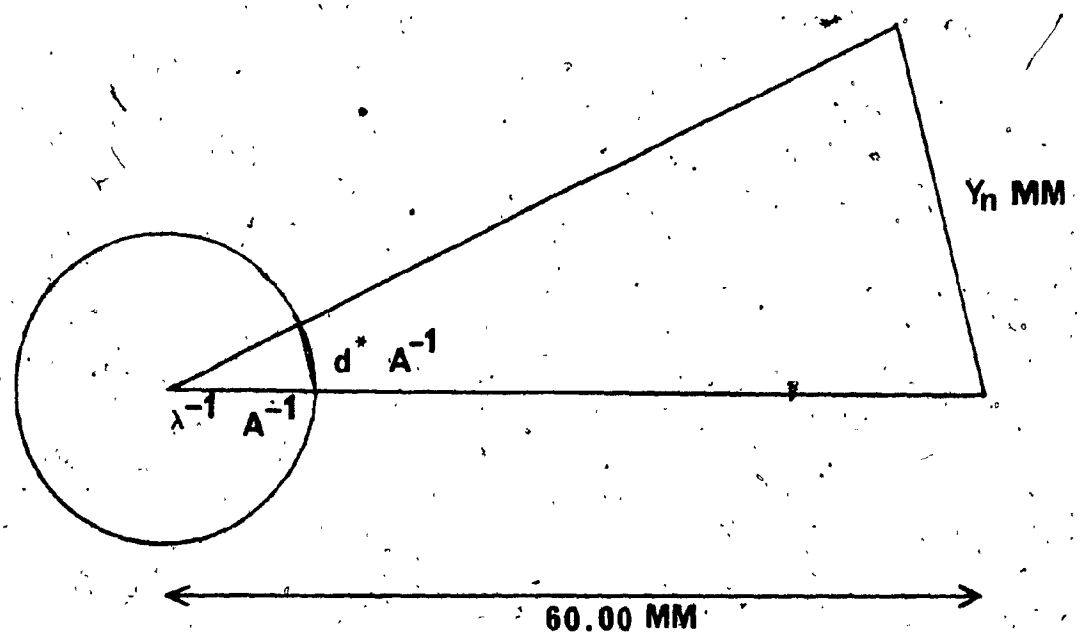


Figure III-16: The relationship of reciprocal space and precession geometry

Data Collection

The Goniometer's arcs were reset to the Weissenberg setting and it was mounted onto the diffractometer such that the small arc faced the X-ray beam and the large arc was parallel to the beam. This position was chosen to establish a zero point in ϕ for the subsequent absorption correction. The ϕ, χ and ω scales were set to zero, while a value corresponding to a strong reflection on one of the axes on the zero-level Weissenberg photograph was set for 2θ. The angle ϕ was scanned until the chosen reflection was located. By scanning 2θ, all reflections belonging to this axis were checked. Similarly, the other axis of the zero-level Weissenberg photograph was located. Two strong reflections were centered using the PDP 8/S computer alignment program supplied by the Picker Nuclear Co. The slits in the receiving collimator were partly shut to ensure higher accuracy during centering. The two centered reflections, in conjunction with the roughly measured unit cell parameters (from the photographs), were used to locate the third axis.

Twelve reflections, strong in intensity and with high 2θ values and evenly scattered over the reciprocal lattice, were chosen and centered at both $+2\theta$ and -2θ values. The accurate 2θ, ω, χ and ϕ values so obtained were averaged appropriately and were used in the least-squares refinement of the approximate cell

parameters, and the orientation matrix. Two reflections which have χ values close to 0° and ϕ separated by 90° were chosen and were used as primary and secondary reflections for the orientation matrix in the refinement process. Estimated standard deviations for the unit cell dimensions were obtained after the second least-squares cycle.

The intensity data were collected using the θ-2θ scan method. A minimum and maximum 2θ value was set and the limits of h, k and ℓ, which determined the portion of the reciprocal cell to be collected, were specified. The length of the scan, needed for low angle reflections, was determined by trial and error. This varies according to the mosaicity of the crystal and the value of 2θ. At high values of $\sin\theta/\lambda$ the difference between the α_1 and α_2 diffraction angles is more pronounced. To allow for this $\alpha_1 - \alpha_2$ dispersion, a factor of 0.692 for Mo K_α radiation was used by the Picker Nuclear data collection program to compute the angular scan length (Base width x 0.692 $\tan\theta$) for every reflection. For the very intense reflections, above 10^4 cps, attenuators with factors of 2.781, 7.959 and 38.190 were automatically inserted in the aperture. A scan rate of 2°/ minute was used. The three reflections chosen as standards, were remeasured every forty or fifty reflections to check the stability of the crystal and the instrument. The data were punched on paper tapes and later copied onto a magnetic tape with the use of a Hewlett Packard 2114 A computer.

Data Reduction

Since the intensities collected constitute only raw data for the structure determination, the preliminary manipulation to convert these into a more usable form is important. This process is referred to as "Data Reduction" and was achieved by using a locally written program called "PREP" (185). The mean atomic scattering factors for all atoms, at intervals of $\sin\theta/\lambda$ of 0.05 Å, were taken from the listing of Cromer and Waber (186) and were used in conjunction with unit cell and space group information as input parameters. The program computes the following information:

1. The program calculates the net intensity and its standard deviation from the raw data according to equations III-2 and III-3, respectively.

$$I = N - [B_1 + B_2]\, t_s / t_b \qquad \text{(III-2)}$$

$$\sigma(I) = \left[N + \frac{(B_1 + B_2)}{2} \left(\frac{t_s}{t_b} \right)^2 + (0.02\,N)^2 \right]^{1/2} \qquad \text{(III-3)}$$

where N is the peak constant in time t_s (seconds) and B_1 and B_2 are the background counts on either side of a peak measured in time t_b (seconds).

The values with $I<3\sigma(I)$ (due to the counting error) were considered unobserved and were not used in the structure solution and refinement process.

2. The program computes relative structure factors and their estimated standard deviation for all the accepted reflection intensities (Equations III-4 and III-5).

$$\left| F_{rel} \right|_{hk\ell} = \left[\frac{I_{hk\ell}}{L_p} \right]^{1/2} \qquad \text{(III-4)}$$

$$\sigma(F_{rel}) = \sigma(I) / (2 . L_p . F_{rel}) \qquad \text{(III-5)}$$

where L_p is a combined term for the Lorentz and Polarization factors and was obtained by application of equation III-6.

$$L_p = \frac{(\cos^2 2\theta_m + \cos^2 2\theta_s)}{\sin^2 2\theta_s (\cos^2 2\theta_m + 1)} \qquad \text{(III-6)}$$

where θ_s and θ_m are the diffraction angles at the sample and monochromator crystals, respectively. The two terms, Lorentz and Polarization factors, can be separately defined as follows:

The Lorentz Factor (L) (187-189)

This is an expression for the time a reciprocal point spends passing through the sphere of reflection. Since the time required for a point in reciprocal space to pass through the space of reflection varies with its position and the direction in which it approaches, the value of L is specific to the diffraction geometry used during the collection of intensity data. A general expression (Equation III-7) for L can be derived for the diffractometer geometry.

$$L = \frac{1}{\sin 2\theta} \qquad \text{(III-7)}$$

At a large Bragg angle (θ) the reciprocal lattice point passes almost tangentially through the sphere of reflection, and L is large. At low Bragg angles, L is again large as the point is near the origin of the reciprocal lattice and the time taken in cutting the sphere of reflection is large. At $\theta = 45^{\circ}$, L is minimum.

Polarization Factor (p) (187-189)

This corresponds to reduction of intensity when X-rays are "reflected" by a crystal plane. The polarization factor which is a simple function of 2θ can be expressed according to equation III-8.

$$p = 0.5 + 0.5 \cos^2 2\theta \qquad \text{(III-8)}$$

At $\theta = 0^{\circ}$ or 90°, there is no polarization and p is 1. When $\theta = 45^{\circ}$, the reflected beam is completely plane polarized and the value of p corresponds to 0.5. This formula is applied once at the monochromator and once at the sample.

3. The program calculates an overall thermal parameter and absolute scale factor according to equation III-9.

$$\ln\left(\frac{\bar{I}_{rel}}{\sum_{i=1}^{N} fo_i^2}\right) = \ln C - 2B\,(\,\mathrm{Sin}^2\theta\,)/\lambda \qquad \text{(III-9)}$$

where $|\bar{I}_{rel}|$ is the average $|F_{rel}|^2$, fo_i is the mean atomic scattering factor for the i^{th} atom and N is the total number of atoms in a unit cell. The slope of the straight line plot, known as Wilson Plot (190), of $\ln(\bar{I}_{rel} / \sum_{i=1}^{N} fo_i^2)$ vs. $(\mathrm{Sin}^2\theta/\lambda^2)$ gives B, while the constant C is obtained as the intercept at $\mathrm{Sin}^2\theta/\lambda = 0$. The latter is later used in scaling the relative structure factors onto an absolute scale according to equation III-10.

$$|F_{abs}| = \frac{|F_{cal}|}{C} \qquad \text{(III-10)}$$

The printed output from the program contains a complete listing of indices of each plane, the value of Sin θ/λ, the observed structure factor, F_{obs}, and σ for each F_{obs}.

Phase Solution

Since the data computed by "PREP" represent only structure factor amplitudes, not the phase associated with them, an electron density distribution map can not be calculated. To overcome this problem, the following two methods, of which one was successfully used, may be employed.

1. The Heavy-atom Method

This method uses a heavy atom, whose contribution to the structure factors outweighs those from the lighter atoms, to allocate an initial set of phases. A Patterson synthesis (191,192) which provides a vector map of the contents of the unit cell, was calculated using the program called "FORDAP" (193), according to equation III-11:

$$P_{(x,y,z)} = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell} |F_{hk\ell}|^2 \cos 2\pi(hx + ky + \ell z) \qquad \text{(III-11)}$$

This expression is known as a Patterson function. The symbol P is

the "density" on the map at coordinates x,y,z, V is the volume of the three dimensional unit cell, and hkℓ are the indices of the reflecting planes of the crystal.

The use of $|F_{(sharp)}|^2_{hk\ell}$ instead of $|F_{hk\ell}|^2$ in equation III-11 produces a so called 'Sharpened Patterson Function' which minimises the overlapping of the peaks due to the diffuse nature of the atoms in space. The relationship between $|F_{(sharp)}|^2_{hk\ell}$ and the observed data can be represented by equation III-12:

$$\left[F_{(sharp)}\right]^2 = \frac{\left[0.1667 + (\sin^2\theta)/\lambda^2\right]\left[F_{obs}\right]^2_{hk\ell}}{\left[\sum_{i=1}^{N} fo_i\right]^2 e^{-B\,(\sin^2\theta)/\lambda^2}} \qquad \text{(III-12)}$$

The term B is the overall thermal parameter predicted by "PREP", and fo_i is the mean atomic scattering factor for the i^{th} atom.

Some characteristics (194) of Patterson maps are:

1. The peaks on the vector map correspond to interatomic vectors.

This information (195) is used to locate the position of heavy atoms in the cell.

2. If there are N atoms in the unit cell, N^2 peaks appear on the vector map.
3. N of these peaks correspond to the vectors between each atom and itself and these occur at the origin of the vector map; the remaining N(N-1) peaks are "useful". The program normalizes the output to 999 as the largest sum at the origin.
4. The intensity of a Patterson peak resulting from vectors between atoms 1 and 2 is 999 times the ratio $z_1 z_2 / \sum_{i=1}^{N} z_i$; where N is the number of atoms in the unit cell.
5. The Patterson function is centrosymmetric, so every peak on the vector map is related to a similar peak by a centre of symmetry.

Direct Methods (196-201)

Though an attempt to solve the structure of (4-ethoxyphenyl)tellurium tribromide using this method was unsuccessful, it is perhaps worthwhile to describe in brief the principles and the programs involved in the method.

This method depends only on the mathematical relationships between phases and the associated probabilities. The

programs employed were "EGEN", "MULTAN" and "FFT" (202).

"EGEN" calculates normalized structure factors (203) according to equation III-13.

$$E^2_{hk\ell} = \frac{|F_{hk\ell}|^2}{\varepsilon \sum_{i=1}^{N} f_i^2} \qquad \text{(III-13)}$$

where $|F_{hk\ell}|^2$ is the square of the structure factor (supplied by "PREP"), ε is an integer which has a value usually 1 but may assume other values for special sets of reflections in certain space groups (204), N is the total number of atoms in a unit cell, and f_i is the atomic scattering factor for the i^{th} atom at the 2θ for the $hk\ell$ reflection involved. The program normalizes the E's (i.e. av $E^2 = 1$) and prints out a list of both experimental and theoretical values for ranges of E vs. 2θ which can be used to assign the crystal symmetry as centrosymmetric or non-centrosymmetric.

"MULTAN" consists of three section: SIGMA2, CONVERGE and FASTAN. SIGMA2 finds $\sum 2$ phase relationships of the form $\phi_{hk\ell} \approx \phi_{h'k'\ell'} + \phi_{h-h',k-k',\ell-\ell'}$ for all $|E_{hk\ell}|$ values. A weight, $K_{hk\ell,h'k'\ell'}$, given to each value can be represented by equation III-14:

$$K_{hk\ell.h'k'\ell'} = 2\sigma_3\sigma_2^{-3/2}\left|E_{hk\ell} \cdot E_{h-h',k-k',\ell-\ell'}\right| \qquad \text{(III-14)}$$

where

$$\sigma_n = \sum_{i=1}^{N} Z_i^N$$

The $\sum 2$ listing contains all the phase relationships under the heading of the reflection to which they are common, in the order of magnitude of decreasing $K_{hk\ell.h'k'\ell'}$.

CONVERGE, the second section of the program, computes the following information:

1. It determines the type of reflections required to define the origin using space group information.
2. It calculates probable signs of centric reflections which are structure invariants, by application of the $\sum_1$ formula appropriate to a particular space group. The general form of the $\sum_1$ formula is given by the equation III-15:

$$S\left\{E_{2h2k2\ell}\right\} \approx S\left\{\left|E_{hk\ell}\right|^2 - 1\right\} \qquad \text{(III-15)}$$

where $S\{E_{hk\ell}\}$ means sign of $E_{hk\ell}$. The reflections used in this formula to set phase relationship are, in most cases, those with high $E_{hk\ell}$ values.

3. It chooses 'best' reflections from $\sum 2$ listing to define the origin by calculating a quantity, $\langle \alpha^2_{hk\ell} \rangle$, a measure of the reliability with which $\phi_{hk\ell}$ may be determined, using equation III-16:

$$\langle \alpha_h^2 \rangle = \sum_{h'} K^2_{h.h'} + 2 \sum_{h'} \sum_{h''} K_{h.h'} K_{h.h''} \frac{I_1(K_{h.h'})}{I_o(K_{h.h'})} \frac{I_1(K_{h.h''})}{I_o(K_{h.h''})} \qquad \text{(III-16)}$$

where

$$h \neq h' \neq h''$$

$$(h = hk\ell;\ h' = h'k'\ell';\ h'' = h''k''\ell'')$$

The I_1 and I_0 are Bessel functions. The reflection with the smallest estimated $\alpha_{hk\ell}$ is eliminated together with all the phase relationships to which the reflection contributes. The elimination of phase relationships changes the value of $\langle \alpha^2_{hk\ell} \rangle$ of all the reflections involved in the relationships so these are updated and once more the reflection with the smallest estimated $\alpha_{hk\ell}$ is eliminated. As the reflection with smallest $\alpha_{hk\ell}$ is eliminated at each stage, the process converges on that group of reflections which are linked together with strong phase relationships. As the elimination continues, the program examines the remaining reflections to ensure that they contain all the necessary reflections for origin definition. If not, the reflection just eliminated is reinstated and becomes one of the reflections used to define the origin. The convergence map, printed as output, contains a listing of origin defining and starting set reflections and a possible route of phase determination by the tangent formula.

FASTAN, the last section of the program, uses the convergence map and the information passed on from the first step in CONVERGE to determine and refine each starting set of phases according to the following weighted tangent formula (205) :

$$\tan \phi_{hk\ell} \approx \frac{\sum_{h'k'\ell'} W_{h'k'\ell'} W_{h-h',k-k',\ell-\ell'} \left| E_{h'k'\ell'} E_{h-h',k-k',\ell-\ell'} \right|}{\sum_{h'k'\ell'} W_{h'k'\ell'} W_{h-h',k-k',\ell-\ell'} \left| E_{h'k'\ell'} E_{h-h',k-k',\ell-\ell'} \right|}$$

$$\frac{\text{Sin}\,(\phi_{h'k'\ell'} + \phi_{h-h',k-k',\ell-\ell'})}{\text{Cos}\,(\phi_{h'k'\ell'} + \phi_{h-h',k-k',\ell-\ell'})} = \frac{T_{hk\ell}}{B_{hk\ell}}$$

(III-17)

where $W_{hk\ell}$ is the weight associated with the phase $\phi_{hk\ell}$ and can be computed according to the relationship:

$$W_{hk\ell} = \tanh\,(1/2\ \alpha_{hk\ell})$$

where

$$\alpha_{hk\ell} = \left| E_{hk\ell} \right| \left(T^2_{hk\ell} + B^2_{hk\ell} \right)^{1/2}$$

At the initial stage, instead of using these weights the program sets weights for the reflections whose phases are determined by the $\sum_1$ formula at $2|p - 1/2|$ (where p is the probability from the $\sum_1$ determination). All other starting reflections are given unit weight. The weights for reflections whose phases are undetermined are given a zero value.

) "FFT" uses structure factor amplitudes, $E_{hk\ell}$, and the phase associated with them to produce an electron density map by application of equation III-18:

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_\ell E_{hk\ell}\, e^{-2\pi i(hx+ky+\ell z)} \qquad \text{(III-18)}$$

Structure Factor Calculations (205-207)

In order to test the correctness of the position of heavy atom(s) determined from the Patterson synthesis, the structure factors were computed using the program called "SFLS" (208).

The structure factor, $F_{hk\ell}$, can be defined as a quantity which represents the magnitude and phase of diffracted X-ray of order $hk\ell$. The amplitude is determined both by the scattering factors for the individual atoms and by the phase δ. The latter can be expressed in terms of fractional coordinates x_j, y_j, z_j of the atoms in the unit cell contributing to the reflection, such that

$$\delta = 2\pi (hx_j + ky_j + \ell z_j) \tag{III-19}$$

The magnitude of the structure factor is given by equation III-20:

$$\left|F_{hk\ell}\right| = \sqrt{A^2_{hk\ell} + B^2_{hk\ell}} \tag{III-20}$$

where

$$A_{hk\ell} = \sum_j f_j \cos 2\pi(hx_j + ky_j + \ell z_j)$$

$$B_{hk\ell} = \sum_j f_j \text{ Sin } 2\pi(hx_j + ky_j + \ell z_j)$$

The phase angle, $\phi_{hk\ell}$, is calculated using equation III-21.

$$\phi_{hk\ell} = \tan^{-1}\left(\frac{B_{hk\ell}}{A_{hk\ell}}\right) \qquad \text{(III-21)}$$

In the exponential form, the complex quantity $F_{hk\ell}$ is expressed by equation III-22.

$$F_{hk\ell} = \sum_j f_j \, e^{2\pi i(hx_j + ky_j + \ell x_j)} \qquad \text{(III-22)}$$

where

$$f_j = f_{o_j} \, e^{-B(\text{Sin}^2\theta/\lambda^2)}$$

The f_j and f_{o_j} are the scattering factors of the j^{th} atom in the

vibrating and stationary states, respectively.

The output from the structure factor calculation program includes, as a minimum for each reflection, the indices, the the observed and scaled structure amplitude $|F_{obs}|$, the calculated structure amplitude $|F_{cal}|$ and the phase information for F_{cal}. A list of the weighted (R_{WF}) and unweighted (R_F) discrepancy factor values, computed using equations III-23 and III-24, appears at the end of the printed output.

$$R_{WF} = \frac{\sum_{hk\ell} W_{hk\ell} \left[|F_{obs}|_{hk\ell} - |F_{cal}|_{hk\ell} \right]^2}{\sum_{hk\ell} W_{hk\ell} \left[|F_{obs}|_{hk\ell} \right]^2} \qquad \text{(III-23)}$$

$$R_F = \frac{\sum_{hk\ell} |F_{obs}|_{hk\ell} - |F_{cal}|_{hk\ell}}{\sum_{hk\ell} |F_{obs}|_{hk\ell}} \qquad \text{(III-24)}$$

These R values are the measure of the correctness of the atomic positions and hence the degree of correctness of structure.

The 'Goodness of fit' index, (GOF), which represents the deviation in an observation of unit weight, is calculated using equation III-25:

$$GOF = \left[\sum_{hk\ell} \frac{W_{hk\ell} \left(|F_{obs}|_{hk\ell} - |F_{cal}|_{hk\ell} \right)^2}{n - m} \right]^{1/2} \qquad \text{(III-25)}$$

where n and m are number of observations and variables, respectively.

Fourier Synthesis (209-211).

The output from the structure factor calculation program serves as the input for a Fourier synthesis. The latter was computed using the program called "FORDAP" (193) to reveal the position of lighter atoms. Based on the assumption that the scattered rays are dominated by the effect of the heavy atom, the calculated

phases were allocated to every observed structure factor. The electron density, $\rho_{(x,y,z)}$, is computed using equation III-26:

$$\rho_{(x,y,z)} = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell} F_{hk\ell}\, e^{-2\pi i(hx + ky + \ell z)} \qquad \text{(III-26)}$$

The approximate coefficients of the Fourier series are known. The limits of x, y, and z are set (usually to encompass an asymmetric unit only) and summation points are chosen to ensure a sufficient resolution. The electron density is calculated at a grid of points in the cell rounded an integer, scaled to 999 as the largest sum, and printed out.

A second Fourier function of importance is the so-called difference synthesis or difference Fourier. It was computed using the same program. The coefficients used were ΔF's which are simply the difference in the observed and calculated structure factors (Equation III-27):

$$\Delta\rho = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell} \Delta F \, e^{i\phi} \, e^{-2\pi i(hx + ky + \ell z)}$$

$$|\Delta F| = (|F_{obs}| - |F_{cal}|)$$

(III-27)

The map represents the difference in the electron density between a Fourier synthesis computed using F_{obs} (observed structure factor) with phases of F_{cal} (calculated structure factor) and a Fourier synthesis using F_{cal} with calculated phases. It shows atoms which have not been included in the structure factor calculation but are present in the structure.

Least-squares Refinement

The least-squares refinement of the scale factor, atomic coordinates and thermal parameters is achieved using the program called "SFLS" (208).

In the initial stage of refinement, each atom is allotted an isotropic vibration parameter, B_j, applied as in

equation III-28:

$$F_{cal} = \sum_j fo_j \, e^{-B_j(\sin^2\theta/\lambda^2)} \, e^{2\pi i(hx_j + ky_j + \ell z_j)}$$

(III-28)

B_j is also called the isothermal parameter and the vibration considered is spherical. In the anisotropic case, this is replaced by six parameters which take into account the amplitude and orientation of a "vibration ellipsoid". The anisotropic thermal parameters, B_{ij}, are applied as shown in the equation III-29:

$$F_{cal} = \sum_j fo_j \, e^{-(h^2\beta_{11} + k^2\beta_{12} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})} \cdot e^{2\pi i(hx_j + ky_j + \ell z_j)}$$

(III-29)

The scattering factors of the heavier elements are corrected for relativistic effects, which arise from the fast movement of the electrons near the nucleus (212):

$$f_{(anom)} = f_o + \Delta f' + i\Delta f'' = f + i\Delta f'' \qquad \text{(III-30)}$$

where f_o is the normal scattering factor, $\Delta f'$ is a real correction term (usually negative), and $\Delta f''$ is the imaginary component. Anomalous dispersion causes the scattered X-ray to be out of phase with the incident rays.

At the end of the refinement, the structure factors are corrected for the extinction effects according to the equation III-31:

$$|F_c| = |F_o| (1 + gI_c) \qquad \text{(III-31)}$$

where g is the secondary extinction coefficient and is characteristic of the crystal. Its value is determined from a plot of I_o/I_c vs. I_c.

Primary extinction relates to an interference process which reduces the intensity of a beam as it passes through a crystal, whereas the secondary extinction coefficient arises for reflections of such intensity that an appreciable amount of the incident radiation is reflected at a given instant by the first planes encountered by the beam. Small crystals suffer less from this effect than large ones.

The function, D, which is minimized in the least-squares analysis is given by:

$$D = \sum_{hk\ell}^{n} W_{hk\ell} \left(|F_{obs}| - |KF_{cal}| \right)^2 \qquad \text{(III-32)}$$

where W is the weight for an observation and is equal to $1/\sigma^2(F)$ and K is the scale factor applied to F_{cal}. Differentiating the right side of the equation III-32 with respect to each of the parameters in turn and setting the derivative equal to zero yields the n normal equations:

$$\sum_{hk\ell} W_{hk\ell}\left(|F_o| - |KF_c(p_1,p_2,..,p_n)| \right) \frac{\partial |KF_c(p_1,..,p_n)|}{\partial p_j} = 0$$

$$(j = 0, 1, .., n)$$

(III-33)

where $(p_1,..,p_n)$ may be scale factor, positional or thermal parameters and the p_j is the j^{th} parameter. These equations are expanded as a truncated Taylor series and in their matrix form become:

$$\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & & & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix} \cdot \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} - \begin{pmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{pmatrix}$$

where

$$a_{ij} = \sum_{hk\ell} W_{hk\ell} \frac{\partial \left| F_{cal} \right|_{hk\ell}}{\partial p_i} \cdot \frac{\partial \left| F_{cal} \right|_{hk\ell}}{\partial p_j}$$

$$x_i = \Delta p_j$$

$$v_1 = \sum_{hk\ell} W_{hk\ell} \left(\Delta F_{hk\ell} \right) \cdot \frac{\partial \left| F_{cal} \right|_{hk\ell}}{\partial p_i}$$

(III-34)

The x_i are the shifts which must be added to the p_i's to obtain improved parameters.

The estimated standard deviations for the positional and thermal parameters were calculated according to the equation III-35:

$$\sigma(pi) = \sqrt{b_{ii} \left[\sum_{hk\ell} W_{hk\ell} \Delta F^2_{hk\ell} \right] / (m - n)}$$

(III-35)

where b_{ii} is the i^{th} diagonal element of the inverse matrix, m the number of observations, and n the number of parameters.

The program "SFLS" has the option of separating the matrix into nine sub-matrices, depending on the number of variables used in the refinement. The total number of variables are determined as the sum of three variables for positional coordinates plus six for the anisothermal parameters of each atom plus one for the scale factor. The maximum number of parameters, which the program can accommodate, is about 200.

The positional and isotropic thermal parameters were refined until no further change in the discrepancy indices was obtained in consecutive cycles. The isothermal parameters were then converted to anisotropic parameters and refinement was continued to a new convergence. In addition to there being no change in the discrepancy indices, no positional parameter shift exceeded 1/10 of its standard deviation. A value of about 5% for the discrepancy indices indicates success of the process and the correctness of the structure.

Geometry (213)

The bond distances and angles were calculated using a program called "UTILITY" (214). The estimated standard

deviations for bond lengths, $\sigma\ell$, and angles, $\sigma\theta$, were calculated according to the equations III-36 and III-37, respectively:

$$\sigma(\ell) = \sqrt{(\sigma^2 x_1 + \sigma^2 x_2)(\Delta x/\ell)^2 + (\sigma^2 y_1 + \sigma^2 y_2)(\Delta y/\ell)^2 + (\sigma^2 z_1 + \sigma^2 z_2)(\Delta z/\ell)^2} \qquad \text{(III-36)}$$

where σx_1 and σx_2 are the estimated standard deviations in the x coordinate of atoms 1 and 2, respectively. ℓ is the bond length.

$$\sigma(\theta) = \sqrt{\sigma_2^2/(\ell_{12})^2 + \sigma_1^2(\ell_{23})^2/(\ell_{12})^2(\ell_{13})^2 + \sigma_3^2/(\ell_{13})^2} \qquad \text{(III-37)}$$

where σ_1, σ_2, and σ_3 are the average isotropic standard deviations of atoms 1, 2 and 3, respectively.

Crystal Structure Illustration

The plots of the molecular structures and the packing diagrams, as "ball and stick" type, with spheres, or thermal-motion probability ellipsoids at the atomic sites were prepared by the program "ORTEP" adopted for the CDC Computer (215). Plotting was performed on a Complot DP X-5 (X-Y) plotter driven by a H.P. 2114A computer.

Data Collection, Structure Solution and Refinement of (4-EtOPh)$TeCl_3$

The crystal chosen (ca. 0.15 X 0.15 X 0.15 mm) had been recrystallized from glacial acetic acid by slow cooling. The zero- and first-level photographs showed mmm symmetry, indicating an orthorhombic lattice type for the compound. The two axes on the zero level Weissenberg photograph were arbitarily named a* and b*.

The Goniometer head was transferred to a Precession camera and the azimuthal angle was set to the value corresponding to the axis a*, on the zero layer Weissenberg photograph. After aligning the crystal, the zero and first level precession photographs comprising h0ℓ and h1ℓ zones were recorded. Similarly, by setting the azimuthal angle value to correspond to the b* axis, the zones 0kℓ and 1kℓ were obtained. The systematic absences were $\ell = 2n+1$ on 00ℓ and $h = 2n+1$ on h0ℓ, which indicated the presence of a 2_1 screw axis parallel to c and a glide plane a perpendicular to axis b. Thus $P2_1am$ and Pma2 were assigned as possible space groups for the compound. Solution of the Patterson was possible only assuming space group $P2_1am$ (see below).

A measurement of the spacing between (10,0,0) and $(\bar{1}0,0,0)$, (0,9,0) and $(0,\bar{9},0)$, and (0,0,6) and $(0,0,\bar{6})$ gave a

Y_a distance of 3.175 mm, a Y_b distance of 3.611 mm and a Y_c distance of 5.725 mm. These correspond to the reciprocal dimensions of 0.07446, 0.08467 and 0,17467 for a*, b* and c*, respectively. The direct cell parameters a = 13.43, b = 11.81, and c = 7.45 Å were obtained using the relationships shown in equation III-38:

$$a = \frac{1}{a^*} \quad ; \quad b = \frac{1}{b^*} \quad ; \quad c = \frac{1}{c^*} \qquad \text{(III-38)}$$

The density calculated on the basis of four molecules per unit cell was 2.01 g cm^{-3} and the experimentally determined value by flotation in methylene bromide and ethylene bromide was 2.011(1) g cm^{-3}. The molecular volume was calculated to be 1173.12 $Å^3$.

The Goniometer head was subsequently transferred to the diffractometer. The reflections (8,0,0), (0,7,0) and (0,0,6) were first located manually and then centered automatically. The twelve reflections selected for least-squares refinement were (0,9,0), (0,$\bar{9}$,0), (10,0,0), ($\bar{10}$,0,0), (8,0,4), (8,0,$\bar{4}$), ($\bar{8}$,0,4), ($\bar{8}$,0,$\bar{4}$), (0,7,4), (0,7,$\bar{4}$), (0,$\bar{7}$,4) and (0,$\bar{7}$,$\bar{4}$). Two least-squares refinement cycles resulted in the following cell parameters;

$\underline{a}$ = 13.427(3), $\underline{b}$ = 11.767(2), $\underline{c}$ = 7.425(2) Å; α = β = γ = 90.0°.

Data collection was initiated using the parameters listed in Table III-4. Of the 1294 reflectons collected 1025 were accepted, 110 were less than 3σ and 19 were absent. Since the crystal was accidently destroyed, no absorption correction (μ = 32.63 cm^{-1}) could be applied in the structure solution.

The heavy-atom method was used to solve the structure. A sharpened Patterson was computed using the thermal parameter, 1.581, and the scale factor, 0.962, predicted by "PREP". A resolution of 1/3 Angstrom was chosen for computing one eighth of the unit cell of the Patterson space. The following four major peaks appeared on the map.

Peak height	Coordinate		
	u	v	w
187	0.500	0.170	0.000
172	0.500	0.430	0.000
172	0.110	0.150	0.500
170	0.390	0.300	0.500

For the space group $P2_1am$, the equivalent positions are x,y,z; x,y,$\bar{z}$; x+1/2,$\bar{y}$,z; x+1/2,$\bar{y}$,$\bar{z}$. The vectors derived from these positions between symmetry-related atoms are 0,0,±2z; 1/2,±2y,±2z;

Table III-4

Data collection parameters for (4-EtOPh)$TeCl_3$

Radiation Used		: Mo K_α (λ = 0.71069 Å)	
Pulse height analyzer		: 100 % of Mo K_α peak	
Attenuators		: Used for rates >10,000 cps	
Space group routine used		: None	
maximum h	15	minimum h	0
maximum k	13	minimum k	0
maximum ℓ	8	minimum ℓ	0
maximum 2θ	50.0	minimum 2θ	4.0
Standards used (hkℓ)		: (8,0,0) (0,7,0) (0,0,6)	
Variation in standard		: ± 2% (random)	
Interval		: Every 50 reflections	
Background counting time		: 20 sec	
Total number of reflections collected		: 1294	
Reflections where I> 3σ(I)		: 1024	

1/2,±2y,0. In fact, two peaks (187 and 172) appear on the Harker plane 1/2,v,0 (corresponding to a vector set 1/2,2y,0 between atoms with coordinates x,y,z and x+1/2,$\bar{y}$,z) giving values of the y coordinates for two crystallographically independent tellurium atoms (y_1 = 0.085 and y_2 = 0.215). Since the two tellurium atoms occupy special positions, by assigning x_1 = 0.000 and z_1 = 0.500 the value for x_2 (from vector set 1/2,2y,0) was obtained. The two sets of coordinates for two tellurium atoms, so obtained, were: $\underline{Te}_1$, x_1 = 0.000, y_1 = 0.085, z_1 = 0.500; $\underline{Te}_2$, x_2 = 0.110, y_2 = 0.215, z_2 = 0.000. These were then used for the first structure factor calculation using "SFLS".

A structure factor calculation based on the position of these two tellurium atoms was carried out. For 1024 refections, the discrepancy factor was 23 %. The difference Fourier which followed the structure factor calculation yielded the position of three chlorine atoms.

Another structure factor calculation which was based on two tellurium and three chlorine atoms gave an R index of 14 %. In another difference Fourier map, all the remaining non-hydrogen atoms were located. An observed Fourier was calculated at 1/3 Å resolution and the position of all the atoms earlier located were verified.

At this stage, the least-squares refinement of

all atoms with isotropic thermal motion was initiated. The starting isotropic temperature factors were arbitarily set at 3.0 for tellurium, 4.0 for chlorine and 5.0 for carbon. Anomalous dispersion corrections of $\Delta f' = -0.5$ and $\Delta f'' = 1.1$ for tellurium and $\Delta f' = 0.1$ and $\Delta f'' = 2.2$ for the chlorine atoms were applied. Only one matrix was required for the refinement. The isotropic convergence ($R_F = 7.1$ %; $R_{WF} = 7.5$ %) was attained by the fourth cycle.

The total of 147 parameters were refined anisotropically for both possible enantiomorphs. Six cycles of refinement with the original set of coordinates gave R_F and R_{WF} values of 5.6 and 5.8 %, respectively. At this stage, refinement for the alternative set of coordinates (-x,-y,-z) was initiated. After two cycles, the discrepancy factors, R_F and R_{WF}, converged to 4.9 and 5.6 %, respectively. Complete information on each isotropic and anisotropic cycle is given in Table III-5. In the last anisotropic refinement cycle, the shifts in 147 parameters were smaller than one-tenth of their corresponding estimated standard deviations.

In a final Fourier difference synthesis, no peaks higher than 0.9 Å^{-3} were seen.

The position of all the hydrogen atoms excepting those on methyl groups were calculated with the program "UTILITY"

Table III-5

Structure factor information for (4-ethoxyphenyl)tellurium trichloride

	before refinement	ISO			
		(I)	(II)	(III)	(IV)
Scale factor	1.39	0.9079	0.9108	0.9110	0.9110
Number of matrix	-	1	1	1	1
Total number of parameters	-	72	72	72	72
Number of reflections	1024	1024	1024	1024	1024
"Goodness of fit"	6.9	23.2	4.2	3.8	3.8
R_F	23.1	39.4	8.1	7.3	7.3
R_F (with rejects)	23.0	39.0	7.8	7.0	7.0
R_{WF}	8.0	45.4	8.3	7.5	7.5
R_{WF} (with rejects)	27.8	45.4	8.3	7.5	7.5

Table III-5 (Contd.)

ANISO ⊕ive SET					
(I)	(II)	(III)	(IV)	(V)	(VI)
0.9128	0.9140	0.9140	0.9140	0.9149	0.9150
1	1	1	1	1	1
147	147	147	147	147	147
1024	1024	1024	1024	1024	1024
4.0	3.2	3.1	3.3	3.3	3.1
7.3	6.1	6.0	5.7	5.7	5.6
7.1	5.9	5.8	5.7	5.5	5.6
7.5	6.2	6.1	6.1	5.9	5.8
7.5	6.2	6.2	6.1	5.9	5.8

Table III-5 (Contd.)

ANISO -ive SET	
(I)	(II)
0.9163	0.9163
1	1
147	147
1024	1024
3.2	3.2
6.1	5.6
5.8	4.9
6.1	5.6
6.1	5.6

assuming a C-H bond length of 1.08 Å. These could not be located in the final Fourier difference map as there was considerable random residual density around the refined atoms.

The observed and calculated structure factors and the final positional and thermal parameters with their estimated standard deviations are given in Appendix-A (page 172) of this thesis.

Data Collection, Structure Solution and Refinement of (4-EtOPh)$TeBr_3$

(4-Ethoxyphenyl)tellurium tribromide was prepared from the corresponding trichloride by reduction to the ditelluride (71) and reoxidation with bromine (96) in carbon tetrachloride. The yellow product was recrystallized from glacial acetic acid and the crystals suitable for X-ray crystallography were grown from the concentrated solution on slow cooling to room temperature. The crystals were washed with a little dry toluene and dried under vacuum before use.

A crystal of approximate dimensions 0.40 X 0.20 X 0.50 mm was selected. The zero- and first level Weissenberg photographs showed no symmetry (except that required by Friedel's law) and thus the crystal was considered to be triclinic. The two chosen axes on the zero level photograph arbitarily were named b* and c*. Their directions were chosen to be a right hand set (with a*).

The crystal was transferred to the precession camera and the zones h0ℓ, hlℓ and hk0, hkl were recorded. The approximate reciprocal cell parameters $a^* = 0.09937$, $b^* = 0.09400$, and $c^* = 0.09094$ Å were measured. The angles $\beta^* = 80.3$ and $\gamma^* = 84.0^\circ$ were obtained directly by measuring the axial rows of reflections from precession photograph (zero-level). The third angle α^* was found to be 107.6° from Weissenberg photographs. The following relationships were used to calculate the real cell parameters:

$$a = \frac{b^* c^* \sin \alpha^*}{V^*} \; ; \; b = \frac{a^* c^* \sin \beta^*}{V^*} \; ; \; c = \frac{a^* b^* \sin \gamma^*}{V^*}$$

$$\cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}$$

$$\cos \beta = \frac{\cos \alpha^* \cos \gamma^* - \cos \beta^*}{\sin \alpha^* \sin \gamma^*}$$

$$\cos \gamma = \frac{\cos \alpha^* \cos \beta^* - \cos \gamma^*}{\sin \alpha^* \sin \beta^*}$$

$$V = \frac{1}{V^*} = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha \cos\beta \cos\gamma}$$

The values calculated were: a = 10.3622, b = 11.3175, c = 11.8155 Å; α = 70.90, β = 102.47, γ = 99.25°; v = 1271.71 Å^3. The density calculated based on four molecules per unit cell was 2.58, while that measured by flotation in a mixture of methylene bromide and ethylene bromide was 2.61(2) g cm^{-3}.

The crystal was transferred to the diffractometer and the three axes were found by locating the reflections (0,6,0), (0,0,4) and (6,0,0). The twelve reflections which were centered were (2,0,$\bar{5}$), ($\bar{2}$,0,8), (5,0,5), ($\bar{5}$,0,$\bar{5}$), (0,6,0), (0,$\bar{6}$,0), ($\bar{6}$,6,0), (6,$\bar{6}$,0), ($\bar{6}$,0,4), (6,0,$\bar{4}$), (6,0,0) and ($\bar{6}$,0,0). After two cycles of least-squares refinement the following cell parameters were obtained: a = 10.280(4), b = 11.209(8), c = 11.715(6) Å; α = 71.93(5), β = 102.01(5), γ = 99.29(5)°; v = 1271.71 Å^3.

Parameters used for data collection are listed in Table III-6. The ϕ rotation data, later used to monitor the success of the absorption program (216) "GNABS", were collected using the reflection (6,0,0), which had χ near 90°. The angle ϕ was changed by 20° intervals and ω and χ were adjusted to keep the crystal in the reflecting position. The reflection was remeasured at each value of ϕ under the same conditions as the normal data collection except that the scan length was fixed at 2.0. An intensity remeasured in this way shows clearly the effects of absorption. It also indicates a successful absorption correction if its corrected intensity becomes invariant with ϕ.

Table III-6

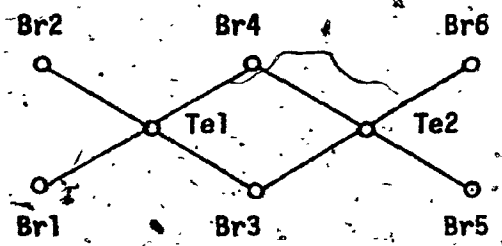
Data collection parameters for (4-EtOPh)$TeBr_3$

Radiation used	: Mo K_α (λ = 0.71069 Å)		
Pulse height analyzer	: 100 % of Mo K_α peak		
Attenuators	: Used for rates >10,000 cps		
Space group routine used	: None		
maximum h	10	minimum h	-11
maximum k	12	minimum k	-11
maximum ℓ	12	minimum ℓ	0
maximum 2θ	45.0	minimum 2θ	4.0
Standards used (hkℓ)	: (6,0,0) (0,6,0) (0,0,8)		
Variation in standard	: ± 2 % (random)		
Interval	: Every 50 reflections		
Background counting time	: 20 sec		
Total number of reflections collected	: 3670		
Reflections where $I > 3\sigma(I)$	: 3136		

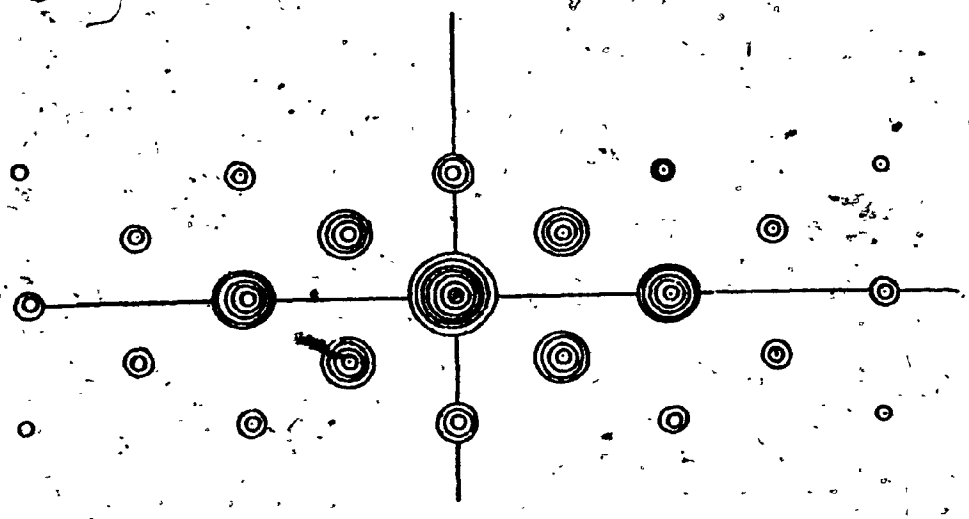
The phase problem was solved by the heavy-atom method. A sharpened Patterson synthesis was calculated for half of the cell at 0.4 Å resolution. A distinct pattern of peaks was observed in the map which suggested a dibromo-bridged dimeric structure for the compound. Careful matching of the peaks on the map with those predicted by such a model (Figure III-17) led to the location of vectors for two tellurium atoms. The coordinates thus found for Te1 and Te2 were 0.250, 0.500. 0.250 and 0.088, 0.350, 0.013, respectively.

A structure factor calculation based on the two tellurium positions gave a discrepancy factor, R, of 63.8 %. The difference Fourier map calculated after one cycle of least-squares refinement (scale factor, coordinates and isotropic thermal parameters — 3.0), provided the position of all six bromine atoms. In the next difference Fourier the remaining non-hydrogen atoms were located. The structure factor calculation which preceeded this difference Fourier gave an R factor of 33.6 %. The absorption correction was applied at this time. Transmission factors obtained ranged from 10 to 12 %.

After five cycles of full matrix refinement, the discrepancy factors, R_F and R_{WF}, had converged to 13.5 and 11.3 %. At this stage, the real and imaginary dispersion corrections for both tellurium ($\Delta f'$ = -0.5, $\Delta f''$ = 2.2) and bromine ($\Delta f'$ = -0.3,



(A)



(B)

Figure III-17: The dimer (A) and the related Patterson peaks (B)

(The size of the circles represents multiplicity of the peaks)

$\Delta f''$ = 2.6) were included and the atoms were divided between two matrices. Anisotropic refinement was initiated. Convergence was obtained in five cycles, giving a final residual of 6.1 % and a final weighted residual of 5.4 %. Two further least-squares cycles including refinement of the extinction parameter gave almost the same values for the R factors. A summary of the refinement is given in Table III-7.

An attempt to locate hydrogen atoms in a final difference Fourier map was unsuccessful. Thus, their positions were calculated using a C-H distance of 1.08 Å (In this Fourier no peak greater than 0.9 e A^{-3} was observed).

The observed and calculated structure factors and the final positional and thermal parameters for the compound are given in Appendix-B (page 182).

Table III-7

Structure factor information for (4-ethoxyphenyl)tellurium tribromide

	Before refinement	ISO				
		(I)	(II)	(III)	(IV)	(V)
Scale factor	0.7730	2.2943	2.3010	2.3195	2.3194	2.3222
Number of matrices	-	1	1	1	1	1
Total number of parameters	-	105	105	105	105	105
Number of reflections	3136	3136	3136	3136	3136	3136
"Goodness of fit"	35.4	8.5	8.6	8.3	8.2	8.1
R_F	64.3	14.0	13.9	13.4	13.3	13.5
R_F (with rejects)	58.1	14.0	13.9	13.4	13.3	13.5
R_{WF}	49.1	11.9	11.8	11.3	11.3	11.3
R_{WF} (with rejects)	49.1	11.9	11.8	11.3	11.3	11.3

Table III-7 (Contd.)

ANISO						
(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
2.3193	2.3267	2.3350	2.3347	2.3123	2.3133	2.3112
2	2	2	2	2	2	2
235	235	235	235	235	235	235
3136	3136	3136	3136	3136	3136	3136
8.3	4.5	4.0	4.0	4.0	4.0	4.0
13.5	7.1	6.2	6.1	6.1	6.3	6.3
13.5	7.1	6.2	6.1	6.1	6.3	6.3
11.3	6.0	5.5	5.4	5.4	5.4	5.4
11.3	6.0	5.5	5.4	5.4	5.4	5.4

APPENDIX A

Table A-1: The observed and calculated structure factors for (4-ethoxyphenyl)tellurium trichloride.

Table A-2: Final positional parameters with estimated standard deviations for (4-ethoxyphenyl)tellurium trichloride.

Table A-3: Final thermal parameters ($x10^4$) with estimated standard deviations for (4-ethoxyphenyl)tellurium trichloride.

Table A-1

The observed and calculated structure factors for (4-ethoxyphenyl)tellurium trichloride

K	L	FOBS	FCAL	SIG
		H = 0		
0	0	2	3	8
0	4	1170	1705	20
0	4	2463	2841	29
0	6	711	735	9
0	8	433	865	12
1	1	650	731	7
1	2	37	49	35
1	3	337	340	6
1	4	161	491	10
1	5	432	454	4
1	6	143	173	10
1	7	144	119	14
1	8	332	373	10
2	0	524	554	6
2	1	1543	1643	16
2	2	1341	1141	11
2	3	1242	1215	12
2	4	240	223	7
2	5	711	750	9
2	6	304	393	8
2	7	427	408	9
2	8	0	71	0
3	0	118	131	7
3	1	61	54	15
3	2	791	807	9
3	3	353	372	6
3	4	37	43	34
3	5	0	25	0
3	6	347	393	8
3	7	237	264	10
3	8	61	64	32
4	0	735	723	8
4	1	811	857	9
4	2	385	419	6
4	3	619	662	8
4	4	253	293	8
4	5	437	526	8
4	6	76	103	19
4	7	242	242	9
4	8	0	24	0
5	0	374	377	6
5	1	1235	1365	14
5	2	82	139	13
5	3	193	336	10
5	4	217	265	9
5	5	314	336	13
5	6	0	52	0
5	7	111	113	9
5	8	47	61	46
6	0	647	652	8
6	1	632	623	8
6	2	673	725	8
6	3	331	413	7
6	4	464	431	8

K	L	FOBS	FCAL	SIG
6	5	350	402	9
6	6	357	387	9
6	7	130	155	16
7	0	1161	1186	13
7	1	225	209	8
7	2	581	614	8
7	3	67	49	22
7	4	745	834	10
7	5	142	163	13
7	6	336	378	9
7	7	43	9	47
8	0	152	166	11
8	1	145	163	11
8	2	339	357	8
8	3	112	124	15
8	4	169	177	12
8	5	68	108	27
8	6	137	140	15
8	7	66	58	30
9	0	508	471	8
9	1	262	262	8
9	2	234	245	10
9	3	284	289	9
9	4	337	326	9
9	5	125	133	16
9	6	144	162	16
10	0	170	187	11
10	1	50	63	36
10	2	504	494	8
10	3	51	15	35
10	4	161	159	12
10	5	8	72	0
10	6	254	289	12
11	0	27	38	63
11	1	424	404	9
11	2	178	144	11
11	3	423	486	9
11	4	53	23	34
11	5	256	244	11
12	0	0	28	0
12	1	434	437	9
12	2	234	219	11
12	3	398	380	9
12	4	67	10	27
13	0	62	34	30
13	1	132	90	16
13	2	432	371	10
13	3	98	84	23
		H = 1		
1	0	1360	1458	5
1	1	742	781	8
1	2	795	695	9
1	3	445	411	6
1	4	985	949	11

K	L	FOBS	FCAL	SIG
1	5	459	456	8
1	6	320	316	8
1	7	164	145	12
1	8	363	376	9
2	0	1272	1374	13
2	1	446	453	6
2	2	1116	1114	12
2	3	147	175	7
2	4	857	853	10
2	5	485	483	7
2	6	443	461	8
2	7	63	70	31
2	8	300	346	10
3	0	1003	1071	11
3	1	1198	1276	13
3	2	492	585	7
3	3	1048	1097	11
3	4	545	568	8
3	5	705	751	9
3	6	226	238	10
3	7	459	526	9
3	8	186	184	12
4	0	699	718	8
4	1	1114	1226	12
4	2	797	824	9
4	3	945	1018	11
4	4	379	416	7
4	5	599	656	9
4	6	318	335	9
4	7	411	460	9
4	8	154	137	14
5	0	813	625	7
5	1	108	92	9
5	2	665	738	8
5	3	147	152	10
5	4	415	451	8
5	5	38	20	44
5	6	271	310	9
5	7	138	82	14
5	8	187	216	13
6	0	1028	1099	11
6	1	578	597	8
6	2	396	413	7
6	3	403	412	7
6	4	664	704	9
6	5	488	440	8
6	6	166	205	13
6	7	172	177	12
7	0	519	529	7
7	1	287	317	7
7	2	501	544	8
7	3	182	211	18
7	4	283	334	9
7	5	204	230	10
7	6	254	278	10
7	7	64	85	28

K	L	FOBS	FCAL	SIG
8	8	491	525	10
8	1	174	173	10
8	2	649	687	9
8	3	192	151	12
8	4	621	666	9
8	5	153	148	13
8	6	378	416	9
8	7	33	91	63
9	0	307	311	8
9	1	289	299	8
9	2	629	646	9
9	3	226	238	10
9	4	268	261	9
9	5	213	227	11
9	6	304	331	10
10	0	117	96	14
10	1	504	477	8
10	2	214	225	11
10	3	476	484	9
10	4	91	99	20
10	5	287	234	10
10	6	115	118	20
11	0	65	93	27
11	1	288	273	9
11	2	212	223	10
11	3	246	229	10
11	4	0	54	0
11	5	283	185	12
12	0	121	113	15
12	1	87	85	24
12	2	186	148	11
12	3	112	116	20
12	4	86	82	24
13	0	183	175	13
13	1	319	263	9
13	2	81	65	27
13	3	223	209	13
		H = 2		
0	0	1696	1888	6
0	1	1452	1689	7
0	2	1134	1056	12
0	3	1113	1059	12
0	4	1158	1107	13
0	5	859	885	10
0	6	521	552	9
0	7	394	396	8
0	8	484	435	9
1	0	778	786	8
1	1	929	853	10
1	2	1276	1162	13
1	3	643	692	8
1	4	588	484	7
1	5	508	475	8
1	6	447	458	8

K	L	FOBS	FCAL	SIG
1	7	266	248	9
1	8	243	233	11
2	0	727	679	8
2	1	844	821	9
2	2	1141	1043	12
2	3	759	706	9
2	4	435	411	7
2	5	497	474	6
2	6	483	462	8
2	7	328	345	9
2	8	170	157	13
3	0	656	662	8
3	1	413	420	6
3	2	1136	1144	12
3	3	398	404	6
3	4	235	212	7
3	5	223	235	9
3	6	451	460	8
3	7	201	208	12
3	8	8	42	0
4	0	1104	1158	12
4	1	693	708	8
4	2	324	324	6
4	3	766	766	9
4	4	668	671	9
4	5	317	311	8
4	6	203	176	10
4	7	346	370	9
4	8	236	236	11
5	0	1051	1093	11
5	1	860	892	10
5	2	486	491	7
5	3	708	741	9
5	4	685	719	9
5	5	532	542	8
5	6	262	293	9
5	7	332	363	9
5	8	249	284	11
6	0	474	520	7
6	1	654	671	8
6	2	682	734	8
6	3	530	542	8
6	4	356	344	8
6	5	385	392	8
6	6	354	374	9
6	7	247	245	10
7	0	1001	1090	11
7	1	506	552	7
7	2	383	431	7
7	3	455	498	8
7	4	666	722	9
7	5	306	346	9
7	6	255	289	10
7	7	223	253	12
8	0	448	456	7
8	1	282	284	9

K	L	FOBS	FCAL	SIG
3	2	414	421	8
3	3	965	948	7
3	4	256	237	8
3	5	174	166	11
3	6	369	345	9
3	7	249	253	11
3	8	90	100	24
4	0	388	406	6
4	1	73	60	13
4	2	1034	1009	11
4	3	146	130	10
4	4	367	346	7
4	5	74	91	22
4	6	467	456	9
4	7	121	108	16
4	8	184	207	13
5	0	1023	1011	11
5	1	208	284	7
5	2	1323	1298	14
5	3	189	179	9
5	4	747	722	9
5	5	167	167	11
5	6	655	636	9
5	7	121	124	18
6	0	417	426	7
6	1	673	686	9
6	2	478	443	7
6	3	616	611	8
6	4	314	305	8
6	5	393	387	8
6	6	279	254	9
6	7	316	306	9
7	0	845	823	7
7	1	891	896	10
7	2	160	151	11
7	3	689	700	9
7	4	285	267	9
7	5	592	602	9
7	6	93	103	20
7	7	328	334	10
8	8	326	326	8
8	1	278	277	8
8	2	108	119	16
8	3	228	213	9
8	4	185	183	12
8	5	211	209	11
8	6	82	86	24
9	0	339	359	8
9	1	368	374	8
9	2	184	183	10
9	3	366	380	8
9	4	255	255	9
9	5	205	203	11
9	6	146	131	14
10	0	137	153	14
10	1	362	347	8
10	2	88	51	22
10	3	333	337	9
10	4	111	113	19
10	5	228	211	11
11	0	512	504	9
11	1	178	158	13
11	2	363	369	9
11	3	137	149	16
11	4	363	381	10
12	0	544	489	9
12	1	110	100	17
12	2	287	267	10
12	3	50	77	40
13	0	269	234	11
13	1	203	204	13
13	2	0	29	0

H = 5

K	L	FOBS	FCAL	SIG
1	0	831	835	9
1	1	1239	1195	13
1	2	412	389	6
1	3	1044	954	11
1	4	530	494	8
1	5	727	687	9
1	6	101	112	19
1	7	439	436	9
1	8	160	180	15
2	0	430	435	6
2	1	863	811	10
2	2	335	388	6
2	3	915	837	10
2	4	290	284	8
2	5	498	458	8
2	6	214	178	18
2	7	489	420	9
2	8	146	123	16
3	0	915	933	10
3	1	313	305	6
3	2	1612	1521	17
3	3	191	174	8
3	4	748	691	9
3	5	146	140	12
3	6	764	736	18
3	7	71	65	27
3	8	324	324	10
4	0	610	615	8
4	1	0	26	0
4	2	1099	1066	12
4	3	56	26	24
4	4	512	500	8
4	5	77	46	22
4	6	605	578	9
4	7	0	29	0
5	0	472	479	7
5	1	451	475	7
5	2	615	595	8
5	3	410	402	7

H = 3

K	L	FOBS	FCAL	SIG
1	0	1125	1125	12
1	1	391	894	11
1	2	776	0??	9
1	3	413	714	9
1	4	397	652	9
1	5	626	597	9
1	6	351	347	8
1	7	361	355	9
1	8	237	242	8
2	0	940	923	7
2	1	1356	1304	11
2	2	1515	1394	16
2	3	935	873	11
2	4	224	217	8
2	5	532	533	8
2	6	541	517	9
2	7	373	336	9
2	8	131	111	15
3	0	965	948	7
3	1	765	703	8
3	2	1477	1398	15
3	3	812	756	9
3	4	645	581	8
3	5	335	314	8
3	6	761	692	10
3	7	362	369	9
3	8	235	265	11
4	0	403	414	6
4	1	650	657	8
4	2	1263	1224	13
4	3	613	592	8
4	4	374	355	7
4	5	366	344	8
4	6	627	637	9
4	7	286	285	10
4	8	158	178	15
5	0	198	208	7
5	1	538	534	7
5	2	531	521	7
5	3	392	402	7
5	4	175	177	10
5	5	345	349	8
5	6	242	244	10
5	7	168	287	14
5	8	48	94	56
6	0	963	998	11
6	1	542	572	7
6	2	148	136	9
6	3	403	408	7
6	4	646	660	9
6	5	380	388	8
6	6	103	101	18
6	7	177	181	13
7	0	514	546	8
7	1	193	188	9
7	2	368	377	7
7	3	279	261	8
7	4	363	376	8
7	5	88	184	24
7	6	149	174	14
7	7	169	162	13
8	0	509	516	8
8	1	665	677	9
8	2	348	347	8
8	3	598	617	9
8	4	363	381	9
8	5	392	418	9
8	6	208	213	11
8	7	296	320	11
9	0	265	276	8
9	1	448	449	8
9	2	328	326	8
9	3	413	416	8
9	4	206	223	11
9	5	267	271	18
9	6	152	155	15
10	0	542	512	9
10	1	173	176	11
10	2	406	405	8
10	3	148	154	13
10	4	383	378	9
10	5	148	132	14
11	0	323	283	9
11	1	267	257	10
11	2	376	332	9
11	3	168	187	12
11	4	238	208	11
11	5	200	172	12
12	0	144	117	15
12	1	60	84	34
12	2	145	138	14
12	3	132	110	16
12	4	122	96	18
13	0	338	297	10
13	1	169	139	13
13	2	227	192	11

H = 4

K	L	FOBS	FCAL	SIG
0	0	1360	1305	14
0	1	1464	1446	15
0	2	1171	1033	12
0	3	1353	1233	14
0	4	673	632	9
0	5	883	836	18
0	6	435	415	8
0	7	977	931	9
0	8	152	154	15
1	0	544	529	7
1	1	1803	952	11
1	2	1305	1173	14
1	3	924	834	18
1	4	251	247	8
1	5	499	475	8
1	6	519	487	9
1	7	378	375	9
1	8	96	87	22
2	0	944	915	10
2	1	316	289	6
2	2	1261	1165	13
2	3	267	256	7
2	4	682	634	9
2	5	206	193	9
2	6	613	583	9
2	7	143	135	15
2	8	256	277	18
3	0	433	414	6
3	1	454	439	6
3	2	820	781	9
3	3	512	486	7

K	L	FOBS	FCAL	SIG
4	4	304	303	4
4	5	327	303	9
4	6	227	191	11
4	7	152	149	11
5	0	403	382	8
5	1	436	457	7
5	2	313	311	6
5	3	354	342	6
5	4	418	408	8
5	5	372	361	6
5	6	245	241	10
5	7	161	157	14
6	0	383	377	6
6	1	201	206	8
6	2	406	374	8
6	3	253	263	9
6	4	243	223	9
6	5	144	141	14
6	6	161	162	14
6	7	165	141	14
7	0	233	231	6
7	1	783	693	9
7	2	341	341	8
7	3	625	611	9
7	4	202	137	13
7	5	445	443	8
8	0	120	152	10
8	1	374	377	8
8	2	455	452	8
8	3	138	135	13
8	4	425	414	9
8	5	242	204	10
8	6	263	274	10
9	0	93	97	33
9	1	477	477	9
9	2	135	135	14
9	3	123	137	9
9	4	62	63	18
9	5	372	365	8
9	6	143	123	15
10	0	334	317	9
10	1	0	14	0
10	2	251	244	10
10	3	63	55	23
10	4	224	234	12
10	5	139	94	22
10	6	97	53	19
10	7	245	130	12
11	0	72	66	28
11	1	232	261	11
11	2	114	63	18

H = 6

K	L	FOBS	FCAL	SIG
0	2	712	636	9
0	4	1126	1049	12
0	6	394	371	8
0	8	981	941	12
0	6	308	298	8
0	7	450	448	9
0	8	213	212	12
1	0	1345	1032	11
1	1	645	667	8
1	2	272	220	7
1	3	604	556	8
1	4	673	627	9
1	5	449	436	8
1	6	165	152	12
1	7	291	247	9
1	8	237	225	12
2	0	1094	1105	12
2	1	716	692	9
2	2	778	721	9
2	3	639	538	8
2	4	794	734	10
2	5	352	327	8
2	6	402	377	9
2	7	259	273	11
2	8	290	298	11
3	0	41	20	26
3	1	451	443	7
3	2	570	554	8
3	3	335	310	7
3	4	103	74	16
3	5	283	260	9
3	6	268	254	9
3	7	136	154	16
4	0	774	784	9
4	1	392	398	7
4	2	801	775	10
4	3	353	339	7
4	4	495	465	8
4	5	231	219	9
4	6	416	398	9
4	7	153	161	17
5	0	944	964	11
5	1	422	435	7
5	2	434	432	10
5	3	425	420	8
5	4	687	668	9
5	5	231	233	10
5	6	495	481	9
5	7	192	208	13
6	0	622	642	8
6	1	584	582	8
6	2	323	336	8
6	3	525	508	8
6	4	453	435	8
6	5	411	392	9
6	6	185	187	12

K	L	FOBS	FCAL	SIG
6	7	271	262	10
7	0	437	443	8
7	1	776	762	10
7	2	319	319	8
7	3	624	608	9
7	4	330	333	9
7	5	511	509	9
7	6	138	166	16
8	0	343	317	8
8	1	120	112	15
8	2	165	168	12
8	3	161	156	12
8	4	243	231	9
8	5	49	54	41
8	6	70	42	28
9	0	385	370	9
9	1	235	234	10
9	2	448	435	8
9	3	204	186	11
9	4	304	277	9
9	5	184	171	12
10	0	113	108	16
10	1	302	300	9
10	2	242	263	10
10	3	288	274	9
10	4	75	66	26
10	5	192	188	12
11	0	277	263	9
11	1	166	177	13
11	2	408	396	9
11	3	72	110	24
11	4	193	218	13
12	0	248	253	10
12	1	198	178	11
12	2	350	324	10
12	3	135	142	17

H = 7

K	L	FOBS	FCAL	SIG
1	0	662	687	8
1	1	549	536	7
1	2	823	795	10
1	3	420	393	7
1	4	511	489	8
1	5	453	430	8
1	6	400	395	8
1	7	188	193	13
2	0	846	909	10
2	1	549	561	7
2	2	516	522	7
2	3	461	445	7
2	4	615	566	9
2	5	364	367	8
2	6	258	253	9
2	7	222	212	11
3	0	1189	1113	12

K	L	FOBS	FCAL	SIG
3	1	741	742	9
3	2	454	437	7
3	3	576	570	8
3	4	785	766	10
3	5	503	497	8
3	6	266	264	9
3	7	270	284	10
4	0	763	803	9
4	1	494	499	7
4	2	508	502	8
4	3	444	429	8
4	4	579	567	9
4	5	361	347	9
4	6	269	270	10
4	7	213	232	12
5	0	527	519	8
5	1	392	409	7
5	2	387	387	7
5	3	422	418	8
5	4	349	372	8
5	5	211	198	10
5	6	139	149	16
5	7	205	208	12
6	0	684	681	9
6	1	493	499	8
6	2	250	247	9
6	3	436	436	8
6	4	443	426	9
6	5	304	307	9
6	6	178	161	13
7	0	7	33	253
7	1	243	232	9
7	2	283	261	8
7	3	110	95	16
7	4	0	41	0
7	5	206	192	11
7	6	157	143	15
8	0	273	283	9
8	1	490	498	9
8	2	568	551	9
8	3	407	396	8
8	4	227	227	11
8	5	346	354	10
8	6	296	303	11
9	0	388	364	8
9	1	313	324	9
9	2	349	342	9
9	3	330	326	9
9	4	285	261	10
9	5	207	199	11
10	0	228	185	10
10	1	271	261	10
10	2	386	362	9
10	3	227	218	11
10	4	173	167	13
11	0	58	78	33

K	L	FOBS	FCAL	SIG
11	1	187	178	12
11	2	307	294	10
11	3	124	147	19
12	0	84	58	24
12	1	110	96	19
12	2	71	80	32

H = 8

K	L	FOBS	FCAL	SIG
0	0	1026	1079	11
0	1	467	457	7
0	2	731	725	9
0	3	355	361	7
0	4	813	780	10
0	5	361	347	8
0	6	465	448	9
0	7	149	173	14
1	0	1106	1145	12
1	1	535	545	8
1	2	570	552	8
1	3	474	470	8
1	4	746	741	10
1	5	299	302	9
1	6	306	313	9
1	7	220	214	11
2	0	618	649	8
2	1	639	642	8
2	2	275	273	7
2	3	598	573	8
2	4	468	464	8
2	5	411	396	8
2	6	124	131	16
2	7	384	299	10
3	0	433	436	7
3	1	289	271	7
3	2	322	301	7
3	3	283	264	8
3	4	298	294	8
3	5	169	158	13
3	6	182	185	12
3	7	124	141	18
4	0	104	87	14
4	1	634	641	9
4	2	339	332	7
4	3	409	394	8
4	4	94	104	19
4	5	491	477	9
4	6	163	166	13
4	7	184	172	13
5	0	433	438	8
5	1	731	727	9
5	2	198	184	10
5	3	564	561	9
5	4	328	299	9
5	5	495	512	9
5	6	121	126	17

K	L	FOBS	FCAL	SIG
0	0	743	774	11
0	1	284	285	9
0	2	479	491	6
0	3	274	275	9
0	4	573	543	9
0	5	214	213	11
0	6	197	200	10
1	0	527	514	9
1	1	200	193	10
1	2	537	583	3
1	3	154	155	14
1	4	421	412	9
1	5	181	184	12
1	6	115	111	13
2	0	73	53	23
2	1	151	141	13
2	2	121	140	16
2	3	232	149	11
2	4	14	50	0
2	5	41	31	24
2	6	307	373	9
3	1	141	172	12
3	2	231	193	11
3	3	214	193	11
3	4	243	263	13
3	5	20	85	44
3	6	343	325	9
4	0	65	90	32
4	2	213	215	11
4	3	64	33	32
4	4	221	237	12
4	5	0	47	0
4	1	325	293	13
4	2	274	250	10
4	3	207	233	11
4	4	70	32	25

H = 9

K	L	FOBS	FCAL	SIG
0	1	193	330	11
0	2	322	224	8
0	3	412	675	9
0	4	263	254	8
0	5	483	468	9
1	0	161	93	17
1	1	164	170	9
1	2	123	137	19
1	3	131	127	11
1	4	163	171	10
1	5	475	483	8
1	6	277	276	8
2	0	694	634	9
2	1	57	47	23
2	2	322	305	9
2	3	137	135	18
2	4	152	188	12
2	5	0	0	0
3	0	804	734	10
3	1	58	63	27
3	2	679	648	9
3	3	161	141	13
3	4	558	537	9
3	5	0	11	0
3	6	331	326	10
4	0	206	203	9
4	1	696	636	9
4	2	60	96	27
4	3	604	589	9
4	4	145	145	13
4	5	466	458	9
4	6	68	41	29
5	0	422	411	8
5	1	46	49	38
5	2	525	509	8
5	3	138	119	14
5	4	294	288	9
5	5	83	31	22
5	6	277	278	11
6	0	118	102	16
6	1	465	380	8
6	2	494	478	8
6	3	312	284	9
6	4	68	95	35
6	5	296	284	10
6	6	278	251	11
7	0	233	244	10
7	1	199	232	10
7	2	185	185	13
7	3	143	149	14
7	4	203	189	11
7	5	136	144	16
8	0	671	662	10
8	1	114	109	16
8	2	486	454	9
8	3	34	74	53
8	4	537	501	9
8	5	106	87	28
9	0	404	402	9
9	1	135	139	15
9	2	146	134	9
9	3	160	152	14
9	4	317	299	11
10	0	52	54	39
10	1	374	356	9
10	2	0	30	0
10	3	328	329	10
11	0	65	74	32
11	1	282	284	13
11	2	114	83	18

H = 10

K	L	FOBS	FCAL	SIG
0	0	583	606	9
0	1	167	176	10
0	2	489	884	11
0	3	94	108	19
0	4	509	503	9
0	5	155	145	12
0	6	450	469	10
1	0	273	241	9
1	1	361	381	8
1	2	571	565	9
1	3	302	283	8
1	4	213	219	11
1	5	281	287	9
1	6	323	312	10
2	0	141	166	13
2	1	557	571	8
2	2	250	268	9
2	3	527	519	9
2	4	159	148	12
2	5	365	374	9
2	6	124	126	18
3	0	389	402	8
3	1	325	348	8
3	2	140	181	13
3	3	207	206	10
3	4	281	284	9
3	5	263	263	10
3	6	83	93	24
4	0	479	482	8
4	1	381	387	8
4	2	152	154	12
4	3	391	361	9
4	4	325	318	9
4	5	256	250	10
4	6	0	84	0
5	0	293	317	9
5	1	651	647	9
5	2	39	75	47
5	3	614	601	9
5	4	243	226	10
5	5	417	396	9
5	6	72	47	28
6	0	415	408	8
6	1	235	235	10
6	2	435	434	9
6	3	262	243	10
6	4	310	312	9
6	5	160	141	14
7	0	483	493	9
7	1	118	104	17
7	2	566	541	9
7	3	130	150	16
7	4	378	381	10
7	5	0	39	0
8	0	259	229	10
8	1	118	105	17
8	2	189	204	14

K	L	FOBS	FCAL	SIG
8	3	66	84	29
8	4	153	146	17
9	0	341	326	9
9	1	184	179	12
9	2	173	196	14
9	3	124	140	17
10	0	332	299	10
10	1	69	59	24
10	2	165	153	13

H = 11

K	L	FOBS	FCAL	SIG
1	0	504	524	8
1	1	348	369	8
1	2	680	695	10
1	3	326	339	9
1	4	398	386	8
1	5	234	230	10
1	6	353	348	10
2	0	154	152	12
2	1	335	350	8
2	2	594	596	9
2	3	337	356	9
2	4	145	152	14
2	5	186	196	12
2	6	334	332	10
3	0	370	387	8
3	1	554	575	9
3	2	254	267	9
3	3	543	538	9
3	4	290	285	9
3	5	343	340	9
3	6	145	147	10
4	0	353	361	9
4	1	386	404	8
4	2	305	332	9
4	3	335	350	9
4	4	265	278	10
4	5	278	289	10
5	0	160	151	12
5	1	138	134	14
5	2	352	357	9
5	3	81	71	24
5	4	92	105	22
5	5	99	131	23
6	0	266	248	9
6	1	203	232	11
6	2	307	315	10
6	3	261	273	10
6	4	213	226	11
6	5	126	119	18
7	0	280	224	12
7	1	155	127	14
7	2	129	156	14
7	3	180	180	14
7	4	183	174	14

H = 12

K	L	FOBS	FCAL	SIG
0	0	209	238	10
0	1	452	478	8
0	2	557	570	9
0	3	494	518	9
0	4	189	194	11
0	5	260	267	11
1	0	67	103	27
1	1	245	240	10
1	2	437	451	9
1	3	207	217	11
1	4	121	114	16
1	5	166	164	14
2	0	484	492	9
2	1	244	269	10
2	2	346	354	9
2	3	227	226	11
2	4	384	379	9
2	5	194	197	13
3	0	311	316	9
3	1	317	333	9
3	2	172	155	12
3	3	243	244	10
3	4	218	208	12
3	5	221	225	12
4	0	319	314	9
4	1	183	207	12
4	2	279	294	9
4	3	212	201	11
4	4	244	236	11
4	5	141	141	17
5	0	349	354	9
5	1	295	304	9
5	2	389	425	9
5	3	299	284	9
5	4	297	285	10
6	0	161	173	14
6	1	285	300	9
6	2	336	325	10
6	3	267	260	10
6	4	152	135	14
7	0	259	278	10
7	1	336	353	10
7	2	267	248	10
7	3	313	315	10
8	0	132	141	10

K	L	FOBS	FCAL	SIG
4	1	114	121	23
4	2	83	92	26
4	3	241	171	12
4	4	151	141	15

H = 13

K	L	FOBS	FCAL	SIG
1	0	283	224	11
1	1	481	450	9
1	2	233	237	11
1	3	421	447	9
1	4	161	157	13
1	5	253	247	11
2	0	83	121	23
2	1	477	411	9
2	2	303	325	3
2	3	123	340	18
2	4	64	78	32
3	0	442	421	9
3	1	193	222	12
3	2	423	434	9
3	3	154	155	14
3	4	378	398	10
4	0	503	528	9
4	1	108	133	19
4	2	264	308	18
4	3	61	64	32
4	4	404	435	10
5	0	0	56	0
5	1	183	238	13
5	2	171	187	14
5	3	149	133	14
5	4	13	52	124
6	0	56	49	34
6	1	138	163	22
6	2	392	392	10
6	3	148	142	17
7	0	78	63	25
7	1	97	116	24
7	2	251	247	12
8	0	146	154	17

H = 14

K	L	FOBS	FCAL	SIG
0	0	150	179	13
0	1	470	497	9
0	2	196	198	12
0	3	445	469	9
0	4	138	113	15
1	0	176	198	12
1	1	239	283	11
1	2	116	134	18
1	3	179	222	14
1	4	159	148	14
2	0	349	378	9
2	1	81	126	26
2	2	216	235	11
2	3	86	113	26
2	4	297	296	10
3	0	251	290	12
3	1	119	146	18
3	2	0	48	0
3	3	84	82	24
4	0	225	255	12
4	1	0	18	0
4	2	285	300	10
4	3	0	45	0
5	0	277	297	11
5	1	68	36	29
5	2	348	358	10
6	0	95	122	23
6	1	251	242	11

H = 15

K	L	FOBS	FCAL	SIG
1	0	0	11	0
1	1	262	288	11
1	2	225	231	12
2	0	71	152	33
2	1	285	300	10
2	2	158	155	14
3	0	468	461	10
3	1	136	127	16
3	2	241	265	12
4	0	368	411	11
4	1	85	101	27

K	L	FOBS	FCAL	SIG
3	3	9207	F36	11
3	5	121	140	35
3	6	146	215	26
3	7	262	360	15
3	11	145	139	27
4	1	177	166	17
4	2	349	366	11
4	3	470	418	11
4	4	242	250	24
4	5	166	169	43
4	6	179	163	30
4	8	542	623	11
4	9	280	312	18
4	11	304	245	19
5	0	462	496	8
5	1	219	213	15
5	2	150	150	24
5	4	1921	1110	10
5	5	1016	949	12
5	6	169	169	35
5	7	201	239	32
5	8	1113	1169	10
5	9	713	768	11
5	11	148	170	41
6	0	981	1001	8
6	1	934	957	8
6	2	142	122	26
6	3	114	89	38
6	4	1202	1144	10
6	5	841	790	11
6	6	268	273	27
6	7	242	199	26
6	8	743	747	12
6	9	446	455	18
6	10	390	441	19
7	0	670	690	8
7	1	327	373	13
7	2	354	406	13
7	3	323	339	15
7	4	576	576	11
7	6	954	956	15
7	7	390	423	19
7	10	444	423	17
8	2	229	232	19
8	3	193	231	25
8	5	199	184	30
8	6	256	204	26
8	7	315	284	24
8	9	159	164	42
9	2	134	130	35
9	3	164	131	30
9	5	183	214	34
9	6	352	354	20
9	7	210	201	35
9	8	161	102	44
10	6	154	64	39

K	L	FOBS	FCAL	SIG
3	7	234	197	31

H = -6

K	L	FOBS	FCAL	SIG
-8	1	207	252	26
-8	2	301	350	14
-7	1	193	156	31
-6	0	266	203	17
-6	1	391	371	12
-6	3	446	455	11
-6	4	242	221	17
-5	0	292	297	16
-5	1	173	179	22
-5	2	741	721	8
-5	3	249	220	16
-5	5	576	550	9
-5	6	466	417	10
-4	1	769	742	8
-4	2	1136	1150	8
-4	3	363	376	10
-4	4	168	157	18
-4	5	317	297	12
-4	6	764	703	8
-4	7	423	255	8
-3	0	211	162	18
-3	1	307	306	11
-3	2	764	774	7
-3	3	382	395	9
-3	5	349	329	10
-3	6	377	367	10
-3	7	185	203	23
-2	0	212	130	19
-2	2	564	573	7
-2	3	351	342	8
-2	4	139	159	19
-2	6	131	106	23
-2	7	172	157	20
-2	8	517	466	9
-2	9	119	70	34
-1	0	331	267	16
-1	3	781	819	6
-1	4	890	911	6
-1	5	149	158	18
-1	6	342	329	10
-1	7	980	996	7
-1	8	796	803	7
0	0	1644	1599	11
0	1	379	345	10
0	2	196	163	12
0	3	1960	1970	10
0	4	1486	1502	8
0	5	163	150	16
0	6	188	136	15
0	7	971	985	7
0	8	796	791	7
0	9	268	243	14

K	L	FOBS	FCAL	SIG
0	10	204	186	20
1	0	1132	1164	7
1	1	384	394	7
1	2	390	386	7
1	3	711	688	6
1	4	722	710	6
1	5	649	674	7
1	6	133	133	21
1	7	240	223	13
1	8	387	365	10
1	9	387	371	11
2	0	143	150	15
2	1	327	325	6
2	2	260	179	18
2	3	115	60	33
2	4	156	129	20
2	5	271	235	12
2	6	267	261	13
2	9	396	374	11
2	10	270	278	17
3	1	251	232	10
3	2	335	329	10
3	3	376	302	16
3	4	308	292	18
3	5	429	416	11
3	6	369	386	11
3	8	356	332	13
3	9	674	691	9
3	10	379	367	13
3	11	140	176	37
4	0	157	157	16
4	1	242	194	12
4	2	108	102	29
4	3	317	285	15
4	4	159	121	40
4	5	766	701	12
4	6	204	276	25
4	7	321	317	15
4	8	423	437	13
4	9	386	424	14
4	10	457	496	13
4	11	405	436	15
5	0	907	912	7
5	3	763	708	8
5	4	1681	1551	11
5	6	485	455	15
5	7	843	827	11
5	8	1039	1076	10
5	10	385	403	15
5	11	247	298	21
6	0	1561	1565	9
6	1	373	383	10
6	2	147	167	24
6	3	757	740	8
6	4	1594	1504	11
6	7	232	192	27

K	L	FOBS	FCAL	SIG
6	8	702	691	12
7	0	859	853	8
7	1	130	38	27
7	2	275	299	14
7	3	134	113	31
7	4	467	402	12
7	5	274	259	22
7	6	196	213	35
7	7	323	329	21
7	9	294	294	23
8	0	164	161	24
8	1	293	311	14
8	2	157	165	26
8	3	121	118	36
8	4	148	64	33
8	5	505	486	13
8	6	152	155	42
8	9	656	692	12
8	10	301	310	23
9	1	446	469	11
9	2	268	257	17
9	3	136	87	34
9	4	129	109	41
9	5	902	907	10
9	6	483	474	15
9	9	784	817	12
10	1	653	701	10
10	2	479	537	12
10	5	732	781	11
10	6	405	440	18
10	7	277	336	27
10	8	174	159	42
11	4	227	262	27
11	5	149	184	45

H = -5

K	L	FOBS	FCAL	SIG
-9	1	313	310	18
-9	2	289	308	19
-8	1	385	398	13
-8	2	402	379	13
-7	1	135	168	31
-7	2	181	124	21
-7	3	415	427	11
-7	4	171	131	24
-6	0	426	405	11
-6	1	297	316	13
-6	2	1160	1207	8
-6	3	949	954	8
-6	6	559	567	10
-6	7	548	522	10
-5	1	380	391	10
-5	2	654	661	7
-5	3	749	761	7
-5	4	147	53	22
-5	5	108	44	31

K	L	FOBS	FCAL	SIG
-5	6	257	255	15
-5	7	361	316	12
-4	0	127	72	26
-4	1	302	169	10
-4	2	138	125	20
-4	3	331	326	9
-4	4	156	178	19
-4	5	246	226	13
-4	6	184	150	18
-4	7	107	91	33
-3	0	542	544	8
-3	1	250	242	11
-3	2	367	376	8
-3	6	197	170	16
-3	7	416	374	9
-3	8	430	404	10
-3	9	128	135	32
-2	0	325	283	11
-2	1	214	215	12
-2	2	581	583	6
-2	3	131	132	16
-2	4	427	408	7
-2	6	324	360	9
-2	7	434	436	9
-2	8	416	413	10
-2	9	160	180	24
-2	10	496	359	8
-1	0	313	257	13
-1	1	133	132	17
-1	2	411	419	6
-1	3	2089	2157	11
-1	4	185	173	12
-1	5	284	303	9
-1	6	597	588	7
-1	7	1365	1326	8
-1	8	349	320	10
-1	9	242	269	15
-1	10	421	401	11
-1	11	353	337	13
0	0	714	671	9
0	1	218	217	11
0	2	882	940	8
0	3	1853	1964	10
0	4	491	481	8
0	6	337	322	8
0	7	768	767	7
0	8	233	256	13
0	9	138	115	24
0	10	131	54	28
0	11	239	237	18
1	0	169	175	10
1	1	327	316	6
1	2	127	49	16
1	3	1105	1119	7
1	4	119	149	18
1	5	292	292	9

K	L	FOBS	FCAL	SIG
1	4	404	415	8
1	7	441	395	8
1	10	297	301	13
1	11	141	93	29
2	0	157	155	11
2	1	142	91	14
2	2	208	203	16
2	3	634	641	8
2	4	387	382	9
2	5	203	163	15
2	8	713	732	8
2	9	340	399	11
2	11	269	231	17
2	12	499	504	11
3	0	479	492	6
3	1	543	543	6
3	2	207	221	14
3	4	1569	1591	11
3	5	1296	1311	9
3	7	269	259	15
3	8	1235	1293	9
3	9	1005	1027	8
3	11	160	145	30
3	12	470	462	13
4	0	1674	1689	9
4	1	1316	1337	8
4	2	256	231	12
4	3	132	40	30
4	4	2304	2049	14
4	5	1533	1412	11
4	6	472	532	11
4	7	196	143	22
4	8	464	497	9
4	9	579	633	10
4	10	556	592	11
4	11	165	161	30
4	12	233	212	25
5	0	1029	1029	7
5	1	737	755	7
5	2	599	597	7
5	3	767	767	6
5	4	552	496	11
5	5	301	238	21
5	6	971	905	10
5	7	417	391	16
5	8	172	156	30
5	10	595	555	11
6	0	104	102	26
6	1	126	144	24
6	2	483	471	9
6	3	123	151	30
6	5	270	216	21
6	6	473	467	14
6	7	426	344	15
6	9	225	229	20
6	11	525	522	14

K	L	FOBS	FCAL	SIG
6	11	422	446	16
7	0	175	135	19
7	1	138	176	25
7	3	311	340	14
7	5	179	227	31
7	6	294	265	22
7	7	461	453	14
7	9	177	166	34
7	10	466	494	15
7	11	469	473	16
8	0	116	132	31
8	3	120	83	34
8	5	270	254	21
8	6	245	206	25
8	7	356	333	19
8	8	465	478	15
8	9	477	514	15
8	11	477	491	16
9	0	292	305	15
9	1	696	721	9
9	2	174	195	25
9	4	717	725	10
9	5	1141	1134	10
9	6	168	236	37
9	7	315	343	23
9	8	574	633	14
9	9	756	829	12
10	0	549	535	10
10	1	935	965	9
10	2	237	266	20
10	4	489	522	13
10	5	754	785	11
10	9	171	211	39
11	1	327	382	17
11	2	207	199	26
11	3	208	231	27
11	6	300	398	24

H = -4

K	L	FOBS	FCAL	SIG
-9	0	212	224	24
-9	1	184	159	26
-8	0	184	226	24
-8	1	401	376	12
-7	0	329	327	13
-7	1	188	214	21
-7	2	770	784	8
-7	3	234	256	14
-7	5	404	393	12
-7	6	805	538	9
-6	1	647	652	8
-6	2	1226	1228	8
-6	3	450	463	9
-6	5	200	204	18
-6	6	568	556	9
-6	7	312	297	14

K	L	FOBS	FCAL	SIG
-5	0	172	124	18
-5	1	186	154	16
-5	2	794	834	7
-5	3	431	477	8
-5	6	313	333	12
-5	7	255	283	15
-4	0	270	267	11
-4	2	642	657	6
-4	3	349	371	8
-4	4	105	129	24
-4	5	165	140	17
-4	6	140	141	22
-4	7	203	202	17
-4	8	299	299	13
-3	0	229	194	11
-3	1	81	80	25
-3	2	169	179	12
-3	3	1059	1083	7
-3	4	1166	1217	7
-3	6	239	211	12
-3	7	946	927	7
-3	8	843	821	7
-2	0	2359	2409	13
-2	1	462	456	8
-2	2	259	227	7
-2	3	1758	1856	9
-2	4	1827	1889	10
-2	5	220	239	11
-2	7	1039	1046	7
-2	8	824	798	7
-2	9	320	306	12
-2	10	132	75	29
-1	0	1502	1393	9
-1	1	610	617	5
-1	2	815	808	5
-1	3	778	773	5
-1	4	748	791	6
-1	5	806	830	6
-1	6	483	488	6
-1	7	260	281	11
-1	8	367	350	9
-1	9	380	354	10
-1	10	174	107	20
0	0	107	109	33
0	1	150	186	10
0	2	414	388	5
0	3	447	428	5
0	4	87	92	20
0	5	268	264	8
0	6	493	495	6
0	7	150	168	16
0	8	140	105	20
0	9	593	620	7
0	10	341	330	12
1	0	70	21	19
1	1	368	357	6

K	L	FOBS	FCAL	SIG
1	2	1269	1301	7
1	3	497	533	5
1	4	77	32	23
1	5	496	491	6
1	6	579	557	6
1	7	134	116	19
1	9	561	564	8
1	10	271	290	14
1	11	223	232	18
2	0	102	26	13
2	1	202	209	9
2	3	652	672	7
2	4	487	503	7
2	5	167	205	15
2	6	376	397	8
2	7	327	352	10
2	8	684	709	7
2	9	175	139	21
2	10	552	533	9
2	11	546	589	10
2	12	496	492	11
3	0	2107	2118	11
3	1	95	78	19
3	2	103	91	25
3	3	1152	1011	10
3	4	2323	2416	13
3	5	160	190	20
3	6	493	501	8
3	7	836	899	7
3	8	1644	1698	10
3	9	193	170	20
3	10	310	348	15
3	11	184	198	26
3	12	560	553	11
4	0	2753	3056	39
4	1	961	952	6
4	2	157	158	16
4	3	1259	1150	9
4	4	2953	2680	16
4	5	205	160	25
4	6	132	134	31
4	8	749	790	9
4	11	208	194	23
5	0	1454	1491	8
5	1	318	305	8
5	2	611	611	7
5	3	167	127	20
5	4	996	921	9
5	5	621	588	11
5	6	148	125	34
5	7	184	173	30
5	9	348	367	15
5	12	197	172	29
6	0	370	354	6
6	1	572	578	7
6	2	174	131	17

K	L	FOBS	FCAL	SIG
6	3	317	308	12
6	4	157	108	26
6	5	876	805	10
6	6	190	154	29
6	8	168	121	32
6	9	855	836	11
6	10	255	283	25
6	12	293	249	22
7	0	133	4	27
7	1	758	773	7
7	2	342	314	11
7	5	1347	1298	10
7	6	950	925	11
7	9	1223	1233	10
7	10	669	674	12
7	11	252	257	26
8	0	136	140	26
8	1	956	980	8
8	2	828	852	8
8	5	1150	1121	10
8	6	603	602	12
8	7	487	507	14
8	8	328	362	19
8	9	522	572	13
8	10	175	184	34
8	11	547	576	14
9	0	313	288	13
9	1	478	498	10
9	2	228	215	18
9	3	496	526	11
9	4	616	638	11
9	5	278	283	21
9	6	141	124	44
9	7	707	736	13
9	8	298	337	21
9	9	157	50	37
9	10	216	219	29
10	0	502	519	10
10	3	357	399	15
10	6	265	262	24
10	7	222	271	33
10	8	347	371	21
10	9	185	196	34
11	4	275	295	22
11	5	191	218	33
11	8	316	347	24

H = -3

K	L	FOBS	FCAL	SIG
-10	0	143	86	36
-10	1	344	347	16
-10	2	283	289	19
-9	1	179	141	25
-9	2	121	155	38
-9	3	434	429	12
-8	0	366	359	12

K	L	FOBS	FCAL	SIG
-8	1	172	185	23
-8	2	736	752	8
-8	3	951	947	8
-8	4	142	86	29
-8	5	153	39	28
-7	1	187	179	19
-7	2	323	317	12
-7	3	526	508	8
-7	6	134	142	32
-7	7	257	227	19
-6	2	104	44	27
-6	3	187	180	16
-6	4	113	96	28
-6	5	170	126	26
-6	6	147	67	30
-5	0	884	885	7
-5	1	510	471	7
-5	2	446	449	7
-5	3	131	117	20
-5	5	227	212	14
-5	6	137	121	24
-5	7	201	151	19
-5	8	240	233	18
-4	0	155	192	15
-4	1	180	151	12
-4	2	776	752	6
-4	3	242	253	10
-4	4	260	238	10
-4	5	141	172	21
-4	7	505	461	8
-4	8	183	164	24
-3	0	90	76	23
-3	1	249	275	7
-3	2	517	488	5
-3	3	2123	2142	11
-3	4	544	519	6
-3	5	208	179	12
-3	6	782	722	6
-3	7	1266	1231	8
-3	9	429	393	10
-3	10	330	311	13
-2	0	1201	1173	7
-2	1	137	105	11
-2	2	1191	1196	7
-2	3	2655	2699	37
-2	4	654	634	5
-2	6	320	291	8
-2	7	1021	942	7
-2	9	316	337	11
-2	9	104	13	32
-2	11	202	185	21
-1	0	137	134	15
-1	1	381	343	5
-1	2	276	269	5
-1	3	1417	1406	8
-1	4	75	101	21
-1	5	156	141	12
-1	7	421	419	7
0	0	232	232	14
0	1	337	312	9
0	2	101	87	11
0	3	812	787	5
0	4	424	427	5
0	6	169	170	12
0	8	693	691	7
0	9	485	476	8
0	11	230	205	18
1	0	701	710	4
1	1	305	286	8
1	2	177	147	9
1	3	102	89	15
1	4	1916	1969	10
1	5	1597	1606	9
1	7	221	200	12
1	8	1497	1514	9
1	9	1206	1176	8
1	10	305	290	13
1	11	132	109	30
1	12	528	510	11
2	0	2268	2334	32
2	1	2103	2092	11
2	2	351	266	12
2	3	169	171	16
2	4	1995	2051	11
2	5	1979	2042	11
2	6	701	718	6
2	7	313	314	10
2	8	839	833	7
2	9	790	779	8
2	10	740	707	8
2	11	170	112	25
2	12	250	247	20
3	0	1256	1205	7
3	1	1176	1167	7
3	2	959	839	7
3	3	1347	1124	10
3	4	277	264	15
3	5	201	170	15
3	6	1234	1227	8
3	7	519	526	8
3	10	746	737	9
4	0	506	437	5
4	1	242	140	8
4	2	861	818	6
4	3	245	164	14
4	5	199	188	24
4	6	407	438	12
4	7	624	620	9
4	9	131	160	32
4	10	522	512	11
4	11	577	571	11
5	0	490	463	6
5	1	133	116	16
5	3	838	781	7
5	5	200	206	24
5	6	343	301	15
5	7	1017	998	10
5	10	478	500	12
5	11	562	601	12
5	12	228	302	27
6	0	166	139	15
6	1	449	436	7
6	2	359	327	9
6	5	780	668	10
6	6	254	268	21
6	7	436	390	13
6	8	485	483	13
6	9	892	846	11
6	11	568	540	13
6	12	430	450	17
7	0	413	396	8
7	1	1326	1294	8
7	2	430	443	9
7	3	196	181	19
7	4	1055	987	9
7	5	2343	2189	13
7	6	411	392	16
7	7	430	428	14
7	8	825	810	10
7	9	1185	1142	10
7	11	311	319	22
7	12	159	185	45
8	0	776	736	7
8	1	2013	2049	11
8	2	424	436	10
8	4	682	620	9
8	5	1538	1498	11
8	8	206	198	27
8	9	475	448	14
8	10	297	286	20
9	0	370	371	12
9	1	497	506	10
9	2	374	366	12
9	3	342	375	13
9	4	165	110	29
9	6	692	714	12
9	7	260	294	26
9	8	148	139	40
9	9	152	149	40
9	10	493	517	14
10	0	200	201	22
10	2	466	488	18
10	5	162	102	36
10	6	557	548	14
11	2	476	479	12
11	6	680	694	13
11	7	279	299	27

H = -2

K	L	FOBS	FCAL	SIG
-10	0	236	252	21
-10	1	318	339	16
-9	0	243	244	18
-9	1	127	174	33
-9	2	761	782	9
-9	3	257	248	17
-8	2	1138	1193	8
-8	3	538	559	9
-8	5	345	344	13
-8	6	476	464	11
-7	1	105	124	29
-7	2	731	764	7
-7	3	400	420	9
-7	4	110	78	30
-7	5	140	98	26
-7	6	381	393	12
-7	7	224	208	20
-6	0	425	448	8
-6	1	352	343	9
-6	2	466	496	7
-6	3	278	282	11
-6	5	140	100	22
-6	6	153	145	22
-6	7	290	260	14
-6	8	244	297	16
-5	0	375	363	7
-5	3	634	642	6
-5	4	946	950	7
-5	6	153	85	20
-5	7	721	693	8
-5	8	814	756	8
-4	0	1942	1992	10
-4	1	496	515	5
-4	3	1656	1675	9
-4	4	1513	1511	8
-4	5	215	232	12
-4	6	176	160	16
-4	7	652	628	7
-4	8	656	610	8
-4	9	285	260	15
-3	0	1668	1728	9
-3	1	477	469	5
-3	2	965	951	6
-3	3	125	110	13
-3	4	782	760	6
-3	5	723	688	6
-3	6	239	226	11
-3	8	210	175	16
-3	9	341	307	11
-3	10	108	20	35
-2	0	73	73	19
-2	1	573	615	4
-2	2	149	152	8
-2	3	514	540	5
-2	5	451	426	6
-2	6	477	466	6
-2	9	380	339	10
-2	10	319	282	12
-1	0	118	77	10
-1	1	684	705	4
-1	2	1432	1316	8
-1	3	667	656	5
-1	4	99	102	14
-1	5	131	100	13
-1	6	577	568	6
-1	7	126	152	19
-1	8	108	86	25
-1	9	378	360	10
-1	10	382	385	11
-1	11	170	226	25
0	0	408	345	6
0	2	185	229	5
0	3	924	912	5
0	4	928	954	6
0	5	309	284	6
0	6	384	396	6
0	7	318	323	8
0	8	987	977	7
0	9	129	47	23
0	10	424	384	10
0	11	445	439	10
1	0	2338	2646	33
1	1	708	544	6
1	2	109	112	11
1	3	1068	1017	6
1	4	3042	3432	43
1	5	648	650	5
1	6	383	401	7
1	7	903	877	7
1	8	1831	1769	10
1	9	426	407	9
1	10	284	291	13
1	11	273	269	15
1	12	480	428	11
2	0	4167	5569	166
2	1	1037	985	6
2	2	178	68	19
2	3	1180	1215	8
2	4	3367	3819	47
2	5	276	288	8
2	7	227	227	12
2	8	1060	1043	8
3	0	2644	2848	37
3	1	578	544	5
3	2	416	363	7
3	4	1194	1160	9
3	5	846	860	7
3	6	157	153	18
3	8	239	222	15

H	L	FOBS	FCAL	SIG
3	9	476	445	9
3	10	122	101	33
3	12	141	156	37
4	0	426	435	5
4	1	1054	1034	6
4	2	296	213	8
4	3	305	277	12
4	4	212	144	22
4	5	1056	905	9
4	6	161	186	24
4	7	266	248	15
4	8	138	94	28
4	9	945	952	9
4	10	490	474	12
4	11	149	162	25
4	12	249	211	22
5	0	107	120	18
5	1	1131	1138	7
5	2	162	145	15
5	5	1648	1722	11
5	6	1061	932	9
5	7	130	93	37
5	8	150	42	27
5	9	1254	1307	10
5	10	782	805	10
5	11	364	368	16
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6	7	702	676	10
6	8	496	521	12
6	9	471	447	14
6	10	302	273	20
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6	12	161	137	37
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7	1	181	141	16
7	2	424	442	9
7	3	794	775	8
7	4	1167	1205	9
7	5	130	76	38
7	6	158	104	36
7	7	1042	1053	10
7	8	296	300	19
7	10	162	236	31
7	11	575	608	13
7	12	122	154	44
8	0	924	955	7
8	1	310	315	12
8	2	296	307	13
8	3	592	602	9
8	4	374	344	13
8	6	267	274	23
8	7	401	410	15
8	8	553	554	12
8	9	306	344	19
8	10	180	185	33
8	11	238	220	26
9	3	153	207	30
9	4	621	630	10
9	5	294	318	19
9	8	531	544	13
9	9	276	325	22
10	0	329	333	14
10	1	304	305	15
10	2	339	361	14
10	3	229	272	22
10	4	213	216	26
10	5	344	358	18
10	6	531	520	14
10	7	169	188	41
10	8	267	297	22
10	9	427	493	17
11	1	274	303	20
11	2	641	628	11
11	3	388	419	16
11	4	156	116	34
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11	7	266	312	28
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-9	3	332	329	13
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-8	1	108	148	32
-8	2	168	134	18
-8	5	179	164	22
-7	0	490	488	8
-7	1	302	339	11
-7	2	449	468	8
-7	3	150	129	20
-7	5	111	57	30
-7	6	134	100	27
-7	7	177	206	24
-6	0	243	225	11
-6	1	101	128	23
-6	2	575	577	6
-6	3	318	311	9
-6	5	395	119	19
-6	6	116	159	29
-6	7	320	293	13
-5	0	126	121	17
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-5	4	737	717	6
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-5	7	1156	1104	8
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-4	4	705	722	6
-4	5	123	111	19
-4	6	314	290	9
-4	7	931	904	7
-4	8	366	363	10
-4	10	193	138	21
-3	0	134	142	10
-3	1	584	592	4
-3	2	598	594	5
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-3	5	117	127	17
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-3	9	185	215	19
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1	10	666	660	8
1	11	214	176	19
2	0	1222	1226	6
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2	2	1041	832	8
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2	6	697	720	6
2	7	881	926	7
2	9	149	125	23
2	10	544	538	9
2	11	555	544	10
2	12	125	148	38
3	0	316	315	5
3	2	465	377	7
3	3	1852	1530	11
3	4	103	16	32
3	5	160	146	17
3	6	133	154	21
3	7	823	875	7
3	9	140	162	26
3	10	302	291	14
3	11	535	508	11
3	12	294	290	18
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4	1	464	448	5
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4	3	313	302	11
4	4	155	104	26
4	5	1042	957	9
4	7	470	493	10
4	8	479	499	10
4	9	1064	1081	9
4	10	156	177	28
4	11	531	519	11
4	12	421	447	14
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5	6	559	551	10
5	7	375	397	14
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5	10	235	208	22
5	11	219	252	26
5	12	198	194	30
6	0	1222	1258	7
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6	7	228	206	21
6	8	214	204	23
6	9	562	549	12
6	10	341	324	18
6	12	203	69	32
7	0	603	617	7
7	1	1232	1249	8
7	2	632	663	7
7	3	558	536	9
7	4	201	167	21
7	5	303	291	17
7	6	948	1000	10
7	7	212	183	23
7	10	613	628	12
8	2	648	681	8
8	3	152	49	26
8	4	260	285	18
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8	8	246	280	22
8	9	157	165	34
8	10	664	680	11
8	11	148	185	41
9	2	608	632	9
9	4	145	194	35
9	6	843	873	11
9	7	391	413	16
9	8	197	194	29
9	9	140	53	39
9	10	569	614	13
10	2	398	434	13
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10	5	250	275	24
10	6	434	426	16
10	7	267	305	25
10	8	418	444	16
10	9	347	359	18
11	0	129	128	37
11	1	445	467	13
11	2	128	171	42
11	4	468	493	14
11	5	579	651	14
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-9	2	580	595	9
-9	3	282	280	15
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-8	3	187	211	19
-8	4	120	102	35
-7	3	496	501	8
-7	4	606	619	7
-7	7	454	436	11
-6	0	1426	1452	8
-6	1	496	471	7
-6	3	792	781	6
-6	4	1097	1090	7
-6	5	119	111	25
-6	7	288	304	14
-6	8	370	343	13
-5	0	1094	1097	7
-5	1	341	343	6
-5	2	654	636	6
-5	3	210	167	11
-5	4	404	394	7
-5	5	519	492	7
-5	6	303	261	11
-5	9	259	202	17
-4	0	70	79	21
-4	1	309	302	6
-4	2	191	137	15
-4	3	688	684	5
-4	5	272	262	9
-4	6	274	218	10
-4	7	104	124	29
-4	8	140	157	25
-4	9	253	234	15
-3	0	112	108	10
-3	1	70	54	16
-3	2	1187	1202	7
-3	3	521	541	5
-3	6	427	424	7
-3	7	195	121	14
-3	9	263	262	14
-3	10	221	196	18
-2	0	366	351	3
-2	1	134	116	6
-2	2	223	224	5
-2	3	734	746	5
-2	4	696	710	5
-2	6	201	193	11
-2	7	366	319	9
-2	8	891	911	7
-2	9	194	223	12
-2	11	234	217	16
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1	8	239	232	13
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1	11	118	102	34
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2	3	243	171	10
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2	6	99	52	23
2	7	324	311	9
2	9	941	926	8
2	10	347	383	12
2	11	281	286	17
3	0	114	108	10
3	1	1300	1241	7
3	2	1298	1099	8
3	3	168	88	23
3	5	1466	2017	11
3	6	1099	1113	8
3	7	384	387	10
3	9	1029	1053	8
3	10	816	841	9
3	11	417	442	13
4	1	1136	1170	7
4	2	1635	1512	9
4	3	111	27	29
4	4	656	602	9
4	5	426	382	11
4	6	1202	1200	9
4	7	684	694	9
4	8	471	518	10
4	9	161	185	28
4	11	710	718	10
4	12	171	169	33
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5	3	917	863	8
5	4	1306	1261	10
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5	11	557	595	12
5	12	202	122	29
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6	4	349	339	13
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6	7	220	198	22
6	8	715	686	10
6	9	251	229	22
6	11	303	272	22
7	1	130	165	23
7	2	175	167	19
7	3	127	79	29
7	4	916	908	9
7	5	476	492	13
7	8	805	849	10
7	9	351	399	17
7	10	193	220	30
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8	2	460	462	10
8	4	228	235	21
8	5	377	379	15
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8	7	165	136	32
8	8	276	287	20
8	9	452	450	14
8	10	633	670	12
8	11	222	214	28
9	1	510	493	9
9	2	1165	1186	9
9	3	501	499	11
9	5	775	776	10
9	6	1410	1429	11
9	7	447	447	14
9	8	201	198	28
9	9	546	572	32
9	10	706	732	41
10	1	648	683	9
10	2	1280	1337	9
10	3	332	394	17
10	5	549	583	13
10	6	828	874	11
10	7	180	195	36
10	8	196	205	31
10	9	176	157	34
11	0	196	189	26
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-8	2	363	393	10
-8	3	226	226	16
-8	6	169	74	25
-7	0	607	617	7
-7	1	299	278	10
-7	2	280	276	11
-7	3	1396	1403	8
-7	4	615	598	7
-7	6	431	403	10
-7	7	775	703	9
-6	0	1219	1258	7
-6	2	796	784	6
-6	3	1947	1962	11
-6	4	650	654	7
-6	6	326	298	11
-6	7	695	651	8
-6	8	239	251	19
-5	0	366	373	6
-5	1	240	254	8
-5	2	234	245	9
-5	3	916	913	6
-5	5	137	136	20
-5	6	198	214	16
-5	7	315	285	12
-5	9	214	138	20
-4	0	293	293	6
-4	1	204	238	8
-4	2	451	464	5
-4	3	297	301	7
-4	4	242	225	9
-4	5	255	245	10
-4	6	368	368	8
-4	8	406	359	10
-4	9	371	364	12
-3	0	310	315	5
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-3	2	212	208	8
-3	3	93	100	16
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-3	5	954	913	6
-3	6	154	171	16
-3	8	753	754	7
-3	9	636	594	8
-3	10	216	217	19
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-2	1	1397	1483	8
-2	2	337	342	4
-2	3	256	258	8
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-2	5	1282	1266	7
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-2	7	392	380	8
-2	8	213	233	14
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-1	2	734	743	4
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-1	7	390	384	7
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1	7	823	840	7
1	9	231	234	15
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K	L	FOBS	FCAL	SIG
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2	2	1242	1006	9
2	3	195	112	13
2	4	1200	1261	9
2	7	218	226	14
2	8	396	421	10
2	9	1064	1025	8
2	10	191	195	23
2	11	160	353	14
3	0	168	142	9
3	1	3954	3466	46
3	2	2021	1816	11
3	3	116	92	33
3	4	1274	1167	9
3	5	2919	3163	15
3	6	706	726	7
3	7	298	294	12
3	8	407	424	8
3	9	1495	1509	10
3	10	261	247	16
4	0	1516	1543	8
4	1	3772	4119	53
4	2	945	937	7
4	3	263	294	15
4	4	1228	1173	9
4	5	3308	3242	18
4	6	132	96	32
4	7	303	280	14
4	8	254	236	18
4	9	679	686	9
4	10	343	305	17
5	0	96	123	24
5	1	1729	1745	10
5	2	779	777	7
5	3	691	632	8
5	4	368	410	13
5	5	203	211	21
5	6	1143	1111	9
5	7	353	323	14
5	8	365	319	15
5	10	474	657	11
5	11	170	120	34
6	0	223	225	11
6	1	275	280	11
6	2	1223	1295	8
6	4	774	794	9
6	5	158	157	31
6	6	945	927	9
6	7	176	173	26
6	8	343	389	16
6	9	147	92	35
6	10	297	290	11
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7	1	104	20	29
7	2	515	510	9
7	3	311	295	14
7	4	297	313	16
7	6	695	647	10
7	8	176	169	29
7	11	263	260	24
8	2	505	449	10
8	3	365	379	13
8	5	427	418	15
8	6	294	350	21
8	7	266	282	21
8	8	472	514	13
8	9	522	562	12
9	1	733	763	9
9	2	298	292	16
9	3	129	118	35
9	4	516	525	12
9	5	819	846	18
9	6	314	328	20
9	7	176	209	33
9	8	605	614	12
9	9	194	180	30
10	0	286	310	17
10	1	716	754	9
10	2	243	313	19
10	4	393	428	16
10	6	260	314	26
10	8	167	180	36
11	2	304	344	19
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11	5	398	421	18
11	6	503	540	15
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-8	4	451	442	10
-8	6	140	109	31
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-7	1	108	104	25
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-7	3	98	99	31
-7	4	188	195	14
-7	5	222	214	16
-7	6	236	225	17
-6	0	107	39	21
-6	1	397	383	7
-6	2	356	368	8
-6	3	637	660	6
-6	5	321	302	11
-6	6	193	162	18
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-5	2	197	177	10
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-5	4	86	27	28
-5	5	209	151	14
-4	0	419	435	5
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-4	4	761	761	6
-4	5	127	142	19
-4	7	269	268	13
-4	8	643	624	8
-4	9	160	166	25
-3	0	2591	2642	36
-3	1	812	817	5
-3	2	222	197	7
-3	3	516	447	5
-3	4	2636	2746	14
-3	5	893	884	6
-3	6	106	75	24
-3	7	531	523	7
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-3	9	388	393	11
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-2	1	1494	1565	8
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-2	3	1016	969	6
-2	4	2463	2635	13
-2	5	511	527	6
-2	6	330	318	8
-2	7	363	365	8
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-1	4	883	906	6
-1	5	610	625	5
-1	6	316	327	8
-1	7	150	176	17
-1	8	165	151	18
-1	9	353	337	11
-1	10	212	188	19
0	0	418	345	6
0	1	1140	1251	6
0	2	444	456	4
0	3	587	618	5
0	5	858	890	6
0	6	66	53	27
0	7	538	546	7
0	9	656	634	8
0	10	372	371	12
0	11	265	254	17
1	0	116	77	20
1	1	1352	1114	9
1	2	739	723	6
1	3	562	574	5
1	5	952	1007	7
1	6	728	721	6
1	7	362	371	9
1	9	603	589	9
1	10	530	515	10
1	11	385	355	13
2	0	66	73	20
2	1	1139	1081	7
2	2	1424	1242	9
2	3	163	166	18
2	4	394	410	8
2	5	420	426	8
2	6	702	740	7
2	7	588	599	8
2	8	525	542	9
2	11	590	560	11
3	0	1625	1727	9
3	1	766	700	6
3	2	894	800	8
3	3	976	916	8
3	4	1537	1445	10
3	5	733	740	8
3	6	137	122	25
3	7	962	1000	8
3	8	387	398	12
3	9	222	212	20
3	10	201	182	23
3	11	506	479	12
4	0	1923	1991	10
4	1	1489	1494	9
4	2	319	306	10
4	3	1005	920	8
4	4	662	619	9
4	7	454	438	11
4	8	585	558	10
4	9	290	286	17
4	11	208	227	27
5	0	365	363	7
5	1	271	296	10
5	2	509	510	8
5	4	558	517	11
5	5	508	518	10
5	6	275	292	17
5	7	225	262	22
5	8	657	669	11
5	9	374	380	16
5	10	205	214	29
6	0	423	448	8
6	1	430	454	8
6	2	693	684	8
6	4	414	452	13
6	5	411	417	14
6	6	970	993	9
6	8	179	238	29
6	9	516	498	12
6	10	769	745	11
6	11	161	179	40
7	1	531	537	8
7	2	1595	1617	10
7	3	676	647	9
7	5	722	720	11
7	6	1249	1799	11
7	7	706	767	10
7	9	557	622	12
7	10	830	828	10
8	1	679	705	9
8	2	1507	1544	10
8	3	609	590	10
8	5	555	548	12
8	6	905	909	10
8	7	179	224	30
8	8	321	352	18
8	9	154	147	36
8	10	208	230	28
9	0	216	244	20
9	1	280	261	16
9	2	451	437	12
9	3	561	586	12
9	4	511	538	13
9	7	705	782	11
9	8	191	220	30
10	0	218	252	22
10	2	163	115	32
10	3	522	567	13
10	4	169	128	31
10	5	413	430	17
10	7	386	436	18
10	8	175	232	35
11	1	253	253	23
11	3	160	213	39
11	4	175	176	37
11	5	316	355	23

H = 3

K	L	FOBS	FCAL	SIG
-11	0	140	32	34
-10	0	172	201	25
-10	1	185	231	24
-10	2	213	237	22
-9	0	377	371	11
-9	2	184	193	21
-9	3	892	887	8
-9	4	366	393	13
-8	0	717	736	7
-8	1	116	74	28
-8	2	201	231	17

K	L	FOBS	FCAL	SIG
-8	3	1084	1078	8
-8	4	402	482	9
-8	5	125	48	32
-7	0	394	394	9
-7	1	133	80	20
-7	2	453	471	6
-7	3	343	358	10
-7	5	230	212	16
-7	6	182	167	22
-6	0	159	139	15
-6	1	86	48	27
-6	2	446	453	7
-6	3	263	276	11
-6	6	122	164	30
-5	0	473	463	6
-5	1	203	212	11
-5	2	189	168	22
-5	3	121	119	19
-5	4	796	810	6
-5	5	464	454	8
-5	6	262	251	13
-5	7	353	330	13
-4	0	502	587	5
-4	1	1590	1593	9
-4	2	271	291	7
-4	3	114	126	18
-4	4	154	154	16
-4	5	965	935	7
-4	6	241	276	11
-4	7	167	125	20
-4	8	145	106	28
-3	0	1214	1204	7
-3	1	644	674	5
-3	2	514	500	5
-3	3	1101	1164	7
-3	4	669	711	6
-3	5	733	709	7
-3	7	432	439	9
-3	8	103	95	33
-2	0	2234	2332	31
-2	1	110	115	11
-2	2	606	631	5
-2	3	637	639	6
-2	4	534	550	6
-2	6	344	329	8
-2	7	110	104	26
-2	8	126	121	25
-2	9	124	100	30
-2	10	224	247	19
-1	0	699	710	4
-1	1	468	470	4
-1	2	67	92	19
-1	3	716	791	5
-1	4	191	197	10
-1	5	179	404	7
-1	6	327	324	8
-1	7	379	345	9
-1	8	141	105	22
-1	9	300	291	13
-1	10	177	158	24
0	0	260	232	11
0	1	872	937	6
0	3	104	106	15
0	5	1136	1160	7
0	6	209	251	11
0	8	363	368	10
0	9	859	865	8
0	10	313	290	14
1	0	150	134	13
1	1	3196	3036	17
1	2	699	723	6
1	4	655	689	6
1	5	2461	2669	13
1	6	741	777	7
1	7	113	86	27
1	8	579	574	9
1	9	1240	1194	9
1	10	317	280	14
2	0	1155	1173	7
2	1	4209	4221	59
2	2	1286	1159	9
2	3	199	212	16
2	4	674	685	7
2	5	2036	2138	11
2	7	324	337	12
2	8	154	152	25
2	9	467	477	11
2	10	203	232	19
2	11	162	166	33
3	0	98	76	20
3	1	1567	1536	9
3	2	821	764	8
3	3	752	642	8
3	4	172	100	24
3	5	246	256	16
3	6	992	1000	8
3	7	322	343	14
3	8	279	259	16
3	10	543	521	11
3	11	178	134	32
4	0	135	192	17
4	2	1396	1313	9
4	3	210	221	22
4	4	791	762	9
4	6	872	832	9
4	7	184	200	26
4	8	556	567	11
4	10	928	902	12
5	0	653	685	7
5	2	992	920	9
5	3	411	340	12
5	4	604	622	10
5	5	667	638	10
5	7	238	162	20
5	8	300	317	19
5	10	368	335	17
6	1	283	290	13
6	2	326	320	13
6	3	474	429	11
6	5	516	515	11
6	6	139	136	33
6	7	230	224	22
6	8	444	436	13
6	9	444	447	14
7	1	1055	1085	8
7	2	673	659	9
7	4	558	568	12
7	5	1142	1144	10
7	6	904	936	12
7	7	177	180	29
7	8	637	679	11
7	9	294	309	20
8	0	360	359	12
8	1	981	1014	9
8	2	617	644	10
8	4	447	474	14
8	5	302	278	20
8	8	192	251	29
8	9	298	299	20
9	2	461	903	13
9	3	326	377	18
9	5	396	430	17
9	6	640	715	13
9	7	219	263	27
10	1	194	209	28
10	2	475	507	14
10	3	292	321	22
10	5	247	232	27
10	6	348	356	20

H = 4

K	L	FOBS	FCAL	SIG
-10	0	484	519	11
-10	1	274	279	17
-9	0	300	288	14
-9	2	382	362	12
-9	3	262	264	16
-8	0	128	140	27
-8	1	132	150	27
-8	2	496	486	9
-8	3	510	504	9
-8	4	136	122	29
-8	5	124	114	35
-7	1	133	96	21
-7	2	117	122	26
-7	3	327	327	11
-7	5	110	96	35
-6	0	356	354	8
-6	1	215	259	13
-6	2	152	136	18
-6	3	185	191	16
-6	4	571	563	8
-6	5	273	246	13
-5	0	1461	1491	8
-5	1	687	686	6
-5	2	243	260	10
-5	3	311	327	9
-5	4	1304	1273	8
-5	5	606	617	7
-5	6	101	8	34
-5	7	343	342	13
-4	0	2781	3057	39
-4	1	883	910	6
-4	2	82	105	25
-4	3	690	698	6
-4	4	1691	1680	9
-4	5	265	257	12
-4	6	239	195	14
-4	7	127	92	28
-4	8	443	430	11
-3	0	2105	2118	30
-3	1	115	63	14
-3	2	271	283	7
-3	4	506	528	7
-3	5	365	353	9
-3	6	130	121	23
-3	7	339	322	11
-3	9	245	218	18
-2	1	968	983	6
-2	2	135	121	12
-2	3	899	886	6
-2	5	599	628	6
-2	6	239	255	12
-2	7	529	535	8
-2	9	365	349	12
-1	1	505	539	5
-1	2	87	80	18
-1	3	193	219	10
-1	5	645	674	6
-1	6	411	411	8
-1	7	199	220	16
-1	8	107	4	32
-1	9	464	464	10
0	1	179	170	11
0	2	764	825	6
0	3	157	157	13
0	4	566	589	6
0	5	136	117	20
0	6	583	592	8
0	7	450	446	9
0	8	492	492	9
0	9	175	125	24
1	0	1552	1393	9
1	1	1413	1229	10
1	2	228	206	13
1	3	576	578	7
1	4	1395	1412	8
1	5	1190	1208	8
1	6	136	159	24
1	7	767	776	8
1	8	425	398	11
1	9	293	293	16
1	10	167	166	25
2	0	2412	2411	13
2	1	1701	1507	10
2	2	159	141	25
2	3	643	611	9
2	4	577	598	6
2	5	306	291	13
2	7	345	351	13
2	8	185	167	24
2	9	172	183	28
3	0	223	194	11
3	1	163	54	21
3	2	676	639	9
3	3	208	219	20
3	4	660	632	9
3	5	532	538	10
3	6	411	423	12
3	8	431	441	12
3	9	347	343	15
3	10	268	272	21
4	0	270	287	11
4	1	663	620	6
4	2	903	810	8
4	3	145	96	32
4	5	417	384	12
4	6	841	798	9
4	7	131	100	36
4	8	227	179	22
4	9	381	382	15
4	10	707	687	11
5	0	167	124	18
5	1	516	493	9
5	2	1521	1450	10
5	3	703	648	10
5	5	646	649	10
5	6	1545	1511	10
5	7	510	516	12
5	9	399	388	16
5	10	699	662	12
6	0	138	100	25
6	1	637	617	9
6	2	1744	1728	11
6	3	601	557	10
6	4	179	129	30
6	5	381	381	15
6	6	967	986	9
6	8	289	304	19
6	9	162	49	31

K	L	FOBS	FCAL	SIG
7	0	330	327	13
7	1	146	83	30
7	2	431	412	13
7	3	582	536	11
7	4	510	574	12
7	5	138	97	37
7	7	727	756	10
7	8	192	206	30
7	9	248	224	23
8	0	226	226	20
8	2	127	111	41
8	3	632	656	11
8	4	150	88	37
8	5	528	566	13
8	7	427	443	15
8	8	181	208	32
9	0	252	224	20
9	1	476	471	13
9	2	134	173	42
9	3	183	149	32
9	4	303	267	21
9	5	394	430	17
9	7	169	173	36
10	1	211	163	28
10	2	149	183	41

H = 5

K	L	FOBS	FCAL	SIG
-10	0	547	535	10
-9	0	238	305	15
-9	2	113	132	38
-8	3	327	287	15
-8	0	198	132	23
-8	2	186	195	21
-8	4	179	156	24
-7	0	116	135	27
-7	4	324	286	13
-7	5	355	305	13
-6	1	626	639	7
-6	2	198	202	15
-6	3	144	152	22
-6	5	341	360	11
-6	6	126	121	32
-5	0	1025	1026	7
-5	1	314	298	9
-5	2	164	178	16
-5	3	739	746	7
-5	4	796	769	7
-5	5	115	90	29
-5	6	369	339	11
-5	7	352	303	13
-4	0	1479	1499	9
-4	1	151	137	14
-4	2	469	395	7
-4	3	532	516	7
-4	4	555	547	7
-4	6	204	190	14
-3	0	480	485	6
-3	1	358	350	6
-3	2	90	104	23
-3	3	146	163	13
-3	5	252	247	13
-3	7	108	172	33
-2	0	167	155	10
-2	1	692	648	5
-2	2	343	351	7
-2	5	737	754	7
-2	8	259	232	15
-1	0	180	175	10
-1	1	1998	2160	11
-1	2	382	429	7
-1	3	176	173	13
-1	4	479	505	7
-1	5	1636	1671	9
-1	6	608	608	7
-1	8	340	370	13
-1	9	643	600	10
0	0	720	671	9
0	1	2677	2755	14
0	2	1057	1078	7
0	3	104	75	24
0	4	585	594	7
0	5	1354	1349	9
0	7	263	234	15
0	8	207	211	21
0	9	325	323	15
1	0	320	257	12
1	1	1186	1057	9
1	2	540	528	8
1	3	713	725	7
1	5	306	331	13
1	6	725	715	8
1	7	311	286	14
1	8	256	193	18
2	0	321	283	10
2	1	299	245	15
2	2	1101	993	9
2	4	507	521	10
2	6	642	700	9
2	8	599	565	10
3	0	558	546	8
3	1	330	267	13
3	2	450	374	13
3	3	444	370	12
3	4	576	546	11
3	5	153	135	31
3	6	307	332	16
3	7	231	231	21
3	8	246	237	20
4	1	433	396	11
4	2	180	255	27
4	3	376	333	15
4	5	488	464	12
4	6	277	219	20
4	8	351	371	18
4	9	469	460	14
5	0	119	-28	30
5	1	1221	1134	9
5	2	1169	1128	9
5	4	467	469	13
5	5	1038	1009	9
5	6	663	659	10
5	7	193	215	29
5	8	500	489	13
5	9	366	371	19
6	0	441	405	11
6	1	1200	1147	9
6	2	726	724	10
6	4	449	453	14
6	5	442	447	14
6	6	170	175	32
6	8	197	153	29
7	0	119	39	37
7	1	180	137	28
7	2	480	482	13
7	3	492	484	13
7	5	356	347	18
7	6	585	622	12
7	7	300	302	20
8	1	329	317	17
8	2	549	538	13
8	3	417	391	15
8	6	341	372	19
8	7	330	355	20
9	2	312	302	20
9	3	547	522	13
9	4	277	276	25

H = 6

K	L	FOBS	FCAL	SIG
-9	2	150	160	31
-8	0	150	161	27
-8	2	187	184	22
-7	0	843	853	8
-7	1	309	315	12
-7	3	216	221	18
-7	4	842	790	8
-6	0	1540	1564	9
-6	1	728	712	7
-6	3	295	297	15
-6	4	813	772	8
-6	5	290	239	15
-5	0	909	912	7
-5	2	312	307	10
-5	4	215	238	17
-5	5	214	204	18
-5	6	250	208	17
-4	0	142	157	16
-4	1	515	510	7
-4	2	99	104	27
-4	3	287	306	11
-4	5	381	376	11
-4	6	171	159	23
-4	7	243	224	18
-3	0	97	26	22
-3	1	224	264	11
-3	3	276	231	10
-3	5	283	273	13
-3	6	315	297	12
-3	7	197	146	20
-2	0	147	150	14
-2	2	424	423	7
-2	3	140	134	19
-2	4	368	379	9
-2	5	204	155	16
-2	6	164	179	22
-2	7	281	245	14
-2	8	350	328	13
-1	0	1117	1164	7
-1	1	1179	1225	7
-1	2	136	113	19
-1	3	346	356	9
-1	4	961	953	7
-1	5	923	916	7
-1	6	164	133	22
-1	7	446	419	10
-1	8	353	320	14
0	0	1695	1598	11
0	1	1540	1524	9
0	2	131	104	22
0	3	490	509	8
0	4	465	463	9
0	5	333	328	12
0	6	141	69	27
0	7	248	231	17
1	0	331	267	14
1	1	161	75	31
1	2	550	540	9
1	3	116	143	32
1	4	152	152	26
1	5	443	468	10
1	6	341	321	13
2	0	204	130	19
2	1	516	470	11
2	2	785	699	10
2	3	136	159	35
2	5	266	302	17
2	6	664	629	9
3	0	201	162	19
3	1	407	380	13
3	2	1251	1162	10
3	3	414	381	13
3	5	464	471	13
3	6	1176	1171	10
3	7	343	349	16
4	1	491	450	11
4	2	1353	1289	10
4	3	567	549	12
4	5	196	183	27
4	6	711	656	11
4	8	322	276	19
5	0	307	297	15
5	2	410	395	14
5	3	534	505	13
5	4	497	507	13
5	6	172	83	30
5	7	598	625	12
5	8	260	264	22
6	0	234	263	20
6	2	150	105	36
6	3	589	570	12
6	5	540	561	13
6	7	330	316	18
7	1	615	601	11
7	2	261	279	22
7	4	189	152	33
7	5	463	455	15
7	6	157	171	38
8	2	234	274	27

H = 7

K	L	FOBS	FCAL	SIG
-9	0	123	100	38
-8	1	388	384	12
-8	2	152	139	29
-7	0	700	690	8
-7	3	464	441	11
-6	0	1025	1001	8
-6	1	145	102	24
-6	2	174	183	21
-6	3	469	440	10
-6	4	430	401	11
-5	0	486	456	8
-5	1	147	184	16
-5	2	122	152	27
-5	4	146	46	26
-5	5	168	162	26
-4	1	509	490	7
-4	3	234	213	14
-4	4	159	110	23
-4	5	468	459	11
-4	6	130	122	33
-3	0	180	172	15
-3	1	1058	1059	7
-3	2	302	289	11
-3	4	334	347	12
-3	5	841	817	8
-3	6	324	307	14
-2	0	354	348	8
-2	1	1610	1659	9

H	L	FOBS	FCAL	SIG
-2	3	429	417	7
-2	3	113	51	27
-2	4	142	140	19
-2	5	753	751	8
-2	7	201	174	22
-1	0	229	231	13
-1	1	482	503	8
-1	2	224	239	14
-1	3	478	492	9
-1	6	414	420	11
-1	7	203	265	18
0	0	300	299	19
0	1	168	178	23
0	2	694	664	8
0	3	152	111	24
0	4	315	290	13
0	6	378	349	13
1	0	428	404	14
1	1	227	201	25
1	2	205	216	23
1	4	376	380	12
1	5	219	153	19
1	6	160	182	29
1	7	143	109	35
2	1	429	385	15
2	2	163	167	35
2	3	216	206	25
2	5	376	361	14
2	6	268	276	19
3	1	1004	911	10
3	2	995	933	10
3	3	188	163	29
3	4	349	329	17
3	5	486	454	10
3	6	414	506	12
-3	7	149	200	30
4	0	316	358	16
4	1	1042	995	10
4	2	747	742	11
4	4	291	301	17
4	5	333	327	16
4	6	432	433	15
4	7	452	437	15
5	5	211	224	28
5	6	494	519	13
6	0	176	74	28
6	2	514	479	13
6	3	292	348	23
6	6	283	292	22
7	0	147	98	36
7	2	247	247	26
7	3	423	417	17
7	4	166	114	39

H = 8

H	L	FOBS	FCAL	SIG
-8	0	695	725	9
-8	1	301	368	14
-7	0	339	362	14
-7	2	141	166	31
-6	0	201	263	20
-6	1	218	240	18
-6	2	186	174	22
-5	2	141	93	26
-5	4	122	31	35
-4	0	177	126	18
-4	2	203	207	18
-4	4	250	233	18
-4	5	186	179	25
-3	0	601	611	7
-3	1	1058	1050	8
-3	3	194	187	20
-3	4	527	524	9
-3	5	633	614	9
-2	0	658	691	7
-2	1	822	798	7
-2	2	182	200	21
-2	3	253	283	15
-2	4	403	418	11
-2	5	208	155	20
-1	0	469	503	9
-1	2	338	342	12
-1	5	226	207	19
-1	6	276	243	17
0	1	299	289	15
0	2	558	572	10
0	3	357	366	13
0	5	213	229	22
0	6	450	467	13
1	0	221	182	27
1	1	290	265	23
1	2	870	864	10
1	3	268	318	20
1	5	310	299	17
1	6	574	593	18
2	0	136	82	39
2	1	178	196	36
2	2	913	859	10
2	3	412	441	16
2	5	175	139	31
2	6	399	383	16
3	0	294	256	18
3	1	328	268	19
3	3	380	357	17
3	4	427	431	16
3	5	145	179	43
4	0	309	272	18
4	3	405	398	17
4	5	249	313	22
5	0	164	145	33
5	1	471	476	14
5	2	310	319	21
5	4	209	166	30
5	5	388	383	17
6	1	203	189	31
6	2	301	279	22

H = 9

H	L	FOBS	FCAL	SIG
-7	0	222	237	21
-6	1	297	284	15
-5	0	112	116	34
-5	1	624	623	9
-5	2	197	208	22
-4	0	114	141	32
-4	1	823	868	8
-4	2	390	405	12
-3	0	261	239	14
-3	1	149	158	25
-3	2	159	174	25
-3	3	314	301	14
-3	4	137	132	31
-2	0	387	406	11
-2	1	250	209	15
-2	2	296	327	13
-1	0	480	495	10
-1	1	151	131	27
-1	2	112	42	36
-1	4	212	233	22
0	1	278	258	18
0	2	120	1[illegible]	39
0	5	274	253	19
1	1	[illegible]1	724	12
1	2	489	484	14
1	4	253	230	21
1	5	520	528	13
2	0	317	269	20
2	1	733	714	12
2	2	692	713	12
2	4	239	263	24
3	2	256	296	28
3	3	346	366	20
4	2	361	341	20
4	3	332	315	21
5	1	184	72	34

H = 10

H	L	FOBS	FCAL	SIG
-5	0	389	392	12
-4	0	559	569	9
-4	1	566	559	10
-3	0	157	186	26
-3	2	201	213	23
-2	1	179	193	23
-2	2	335	381	14
-1	2	421	437	13
0	2	359	405	17
1	0	149	124	49
1	1	238	189	31
2	0	269	282	24
2	1	175	105	42

Table B-2

Final positional parameters with estimated standard deviations (Å)[a] for (4-ethoxyphenyl)tellurium tribromide[b]

Atom	X	Y	Z
Te1	0.2463(1)	0.5073(1)	0.2671(1)
Te2	0.0823(1)	0.3394(1)	-0.0212(1)
Br1	0.1967(3)	0.4642(3)	0.4795(2)
Br2	0.4199(2)	0.6899(2)	0.2797(2)
Br3	0.0368(2)	0.3003(2)	0.2231(2)
Br4	0.2779(2)	0.5496(2)	0.0134(2)
Br5	-0.0920(2)	0.1579(2)	-0.0488(2)
Br6	0.1237(2)	0.3936(2)	-0.2395(2)
C11	0.3852(16)	0.3746(14)	0.3249(13)
C12	0.5019(19)	0.4044(17)	0.2774(15)
C13	0.6058(17)	0.3223(17)	0.3227(15)
C14	0.5835(18)	0.2149(16)	0.4222(16)
C15	0.4650(18)	0.1845(17)	0.4686(16)
C16	0.3663(17)	0.2656(16)	0.4193(14)
C17	0.8225(19)	0.1836(22)	0.4605(20)
C18	0.9042(19)	0.1048(25)	0.5573(25)
O1	0.6825(13)	0.1358(11)	0.4799(11)
C21	0.2376(16)	0.2215(14)	0.0528(14)
C22	0.3547(18)	0.2552(16)	0.0006(17)
C23	0.4621(18)	0.1798(15)	0.0517(16)
C24	0.4472(17)	0.0772(15)	0.1538(15)
C25	0.3316(16)	0.0417(14)	0.2021(15)
C26	0.2236(18)	0.1176(16)	0.1522(15)
C27	0.6774(18)	0.0307(18)	0.1641(19)

Table B-2 (Contd.)

C28	0.7611(18)	-0.0712(19)	-0.2467(19)
O2	0.5504(12)	0.0018(11)	0.2122(11)
H12	0.5151	0.4906	0.2051
H13	0.6959	0.3411	0.2835
H15	0.4499	0.0994	0.5416
H16	0.2754	0.3104	0.3987
H17A	0.8447	0.2804	0.4631
H17B	0.8373	0.1774	0.3741
H22	0.3624	0.3370	-0.0772
H23	0.5527	0.2012	0.0130
H25	0.3226	-0.0428	0.2770
H26	0.1331	0.0946	0.1911
H27A	0.6606	0.0270	0.0711
H27B	0.7248	0.1227	0.1687

a. The estimated standard deviations are right justified to the least significant digits of the fractional coordinates.

b. See Figure III-9, page 108, in the text for a description of the naming scheme used.

Table B-3

Final thermal parameters[a] ($\times 10^4$) with estimated standard deviations for (4-ethoxyphenyl)tellurium tribromide

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te1	111.9(19)	85.8(16)	71.7(14)	17.2(13)	6.0(13)	-41.6(12)
Te2	84.6(17)	65.8(14)	67.1(13)	10.3(12)	11.1(11)	-31.4(11)
Br1	239.7(47)	246.4(45)	85.0(24)	84.6(37)	31.9(27)	-73.3(27)
Br2	180.3(40)	103.5(28)	181.2(34)	-3.6(26)	-21.1(29)	-84.5(26)
Br3	100.0(27)	110.6(25)	81.5(21)	6.9(21)	34.7(19)	-35.4(19)
Br4	123.1(30)	66.3(21)	78.7(20)	-16.8(20)	21.1(19)	-23.0(17)
Br5	98.2(28)	98.8(25)	158.4(28)	-12.1(21)	5.1(23)	-71.0(22)
Br6	174.8(34)	114.9(26)	66.0(19)	40.1(24)	26.2(21)	-24.5(19)
C11	102(24)	73(19)	68(17)	13(17)	30(16)	-35(15)
C12	116(28)	105(23)	79(19)	-19(21)	20(19)	-30(18)
C13	91(25)	117(24)	74(19)	-8(20)	19(17)	-13(18)
C14	89(25)	82(21)	93(20)	22(19)	-10(18)	-39(17)
C15	62(24)	119(25)	105(21)	6(20)	-2(18)	-34(19)
C16	108(26)	102(22)	71(18)	9(19)	12(17)	-39(17)

Table B-3 (Contd.)

C17	47(24)	221(36)	177(30)	50(24)	67(23)	10(28)
C18	50(26)	282(45)	259(40)	8(28)	2(27)	-60(37)
O1	148(20)	117(16)	105(14)	16(15)	13(14)	-11(13)
C21	95(23)	48(18)	68(17)	3(16)	19(16)	-27(15)
C22	108(27)	78(21)	121(22)	2(20)	30(21)	-48(18)
C23	132(28)	47(18)	92(19)	23(19)	34(19)	-8(16)
C24	72(23)	53(19)	97(20)	5(17)	11(18)	-38(16)
C25	63(22)	53(18)	96(19)	1(16)	27(17)	-23(16)
C26	139(28)	61(19)	77(18)	-17(19)	36(18)	-33(16)
C27	74(25)	134(27)	174(28)	-11(21)	72(23)	-17(24)
C28	74(25)	155(29)	186(29)	72(22)	-5(22)	-44(24)
O2	121(18)	84(14)	118(14)	24(13)	7(13)	-26(12)

[a]Anisotropic thermal parameters are applied in the expression exp $(-h^2 \beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2\ hk\beta_{12} + 2\ h\ell\beta_{13} + 2\ k\ell\beta_{23})$. The estimated standard deviations are right justified to the least significant digits of the fractional coordinates.

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